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STUDIES IN THE FRIEDEL-CRAFTS REACTION

Part VII. The Action of Phthalic and Succinic Anhydrides on Resorcinol Derivatives

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(From the Department of Chemistry, St. Xavier's College, Bombay)

Received August 11, 1941

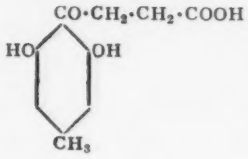
Aromatic hydrocarbons, and phenolic ethers have been condensed with succinic anhydride in the presence of anhydrous aluminium chloride with the formation β-benzoyl-propionic acid derivatives. Ullmann and his co-workers[1] have condensed phthalic anhydride with phenol and its homologues, while Mitter and De[2] and Raval, Bokil and Nargund[3] have condensed the same phenols with succinic anhydride. So far, these anhydrides have not been condensed with di-hydric and tri-hydric phenols, and Dalal and Nargund[4] have reported their failure to condense resorcinol with succinic anhydride.

Desai and (Mrs.) V. H. Shroff[5] have shown that it is possible to condense resorcinol and orcinol with succinic anhydride, though the yield of β-2:6-dihydroxy-4-methylbenzoyl-propionic acid (I) from orcinol was not satisfactory. Moreover, the reaction between oricinol and succinic anhydride gave another instance of γ-substitution which is rare.

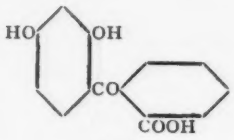
We have now condensed phthalic anhydride with resorcinol itself, as well as its mono and dimethyl ethers, resacetophenone, β-methyl resorcylate, hydroquinone, and pyrogallol, in the presence of anhydrous aluminium chloride. Resorcinol gave a good yield of *o*-2: 4-dihydroxybenzoyl-benzoic-acid (II) which, on Clemmenson reduction gave *o*-2 : 4-dihydroxybenzyl-benzoic acid. Resorcinol monomethyl as well as dimethyl ether gave the same acid, and as it gave positive ferric chloride reaction, it must be *o*-2-hydroxy-4-methoxybenzoyl-benzoic acid (III). Mitter and De[6] have also observed the demethylation of one of the methoxyl groups in the condensation of resorcinol dimethyl ether with succinic anhydride. Resacetophenone, β-methyl resorcylate, hydroquinone, and pyrogallol did not condense with phthalic anhydride.

Finally the bromination as well as the Clemmenson Reduction of β-2:4-dihydroxybenzoyl-propionic acid to γ-2: 4-dihydroxyphenyl-butyric acid was

studied as we required this acid for some other synthetic purpose. The mono- and dimethyl derivatives of the bromo-keto-acid have been prepared, and their constitutions have been determined, as the same acids are obtained by brominating the keto-acids obtained from succinic anhydride and resorcinol mono- and dimehyl-ethers by Dalal and Nargund.[7]



(I)



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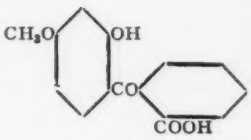

(III)

Experimental

O-2 : 4-*Dihydroxybenzoyl-benzoic Acid.*—To a solution of resorcinol (11 g.) and anhydrous aluminium chloride (27 g.) in nitrobenzene (150 c.c.), phthalic anhydride (15 g.) was slowly added, and the mixture was heated on water-bath for 6 hours after keeping at the ordinary temperature for 48 hours. Having decomposed the aluminium chloride with ice-cold hydrochloric acid, the nitrobenzene was distilled off in steam. The soild that separated out on the addition of sodium chloride to the solution was filtered off. The crude acid, after purification through dissolution in the sodium carbonate solution, crystallised from dilute alcohol in pale-yellow needles, m.p. 202° (yield = 5 gm.). Its alcoholic solution gave wine-red coloration with ferric chloride. [Found: C, 64·7; H, 4·2; $C_{14}H_{10}O_5$ requires C, 65·1; H, 3·9 per cent.]

The *mono-bromo* derivative obtained by adding bromine (0·3 c.c.) in glacial acetic acid (2 c.c.) solution to the acetic acid solution (20 c.c.) of the acid (10·5 g.) crystallised from benzene in plates m.p. 220°. [Found: Br, 23·4; $C_4H_{19}O_5Br$ requires Br, 23·7 per cent.]

Reduction to O-2: 4-*dihydroxybenzyl-benzoic Acid.*—A mixture of the keto-acid (2.g.), amalgamated zinc (10 g.) and dilute (1:1) hydrochloric acid (50 c.c.) was heated on sand-bath under reflux for six hours. The cooled solution was extracted with ether, the solution dried, and the acid recovered. It crystallised from benzene in tiny needles, m.p. 143°. [Found: C, 68·5; H, 5·2; $C_{14}H_{12}O_4$ requires C, 68·9; H, 5·0 per cent.]

Condensation of Resorcinol Monomethyl Ether with Phthalic Anhydride and Formation of O-2–hydroxy-4-methoxy-benzoyl-benzoic Acid.—To a solution of resorcinol monomethyl ether (6·2 g.) and anhydrous aluminium chloride (13·5 g.) in nitrobenzene (7·5 c.c.) phthalic anhydride (7·5 g.) was

slowly added with constant shaking. After keeping at the room temperature for 48 hours, the mixture was heated on the water-bath for two hours. Having decomposed the excess of aluminium chloride with ice-cold hydrochloric acid, the nitrobenzene was steam distilled off, and the solid that separated on cooling was filtered off. After purification through sodium bicarbonate solution, the *acid* crystallised from dilute alcohol in needles, m.p. 165°. Its alcoholic solution gave wine-red coloration with ferric chloride. [Found: C, 65·8; H, 4·5; $C_{15}H_{12}O_5$ requires C, 66·2; H, 4·4 per cent.]

The *mono-bromo* derivative crystallised from alcohol in needles, m.p. 203°. [Found: Br, 22·6; $C_{15}H_{11}O_5Br$, requires Br, 22·8 per cent.]

Condensation of Resorcinol Dimethyl Ether with Phthalic Anhydride and Formation of O-2-hydroxy-4-methoxybenzoyl benzoic Acid.—A solution of resorcinol dimethyl ether (7 g.) phthalic anhydride (7·5 g.), anhydrous aluminium chloride (13·5 g.) in nitro-benzene (75 c.c.) was heated on the water-bath for two hours after keeping at the room temperature for 24 hours. The product worked up in the usual manner crystallised from dilute alcohol in needles, m.p. 165°, undepressed by the acid prepared from presorcinol monomethyl ether (Yield = 3 gm.).

Clemmenson Reduction of β-2: 4-dihydroxybenzoyl Propionic Acid to γ-2:4-Dihydroxyphenyl-Butyric Acid.—The keto-acid was prepared by the method of Desai and (Mrs.) V. H. Shroff (*loc. cit*). Its *mono-bromo*-derivative crystallised from alcohol in needles, m.p. 190°. [Found: Br, 27·5; $C_{10}H_9O_5Br$ requires Br, 27·7 per cent.]

On methylation with dimethyl sulphate in presence of 10 per cent. caustic soda, the mono-bromo acid gave *O-5-bromo-methoxy-2-hydroxybenzoyl-propionic acid*, which crystallised from alcohol in needles, m.p. 203°. [Found: Br, 26·1; $C_{11}H_{11}O_5Br$ requires Br, 26·4 per cent.]

The same *bromo-acid* was also obtained by the bromination of *O*–4-methoxy-2-hydroxy-benzoyl-propionic acid which was prepared by the condensation of resorcinol monomethyl ether with succinic anhydride. When this acid was further methylated with dimethyl sulphate in presence of anhydrous potassium carbonate in acetone solution, the acid, m.p. 179°, and crystallising from dilute alcohol in needles was obtained. Its alcoholic solution did not give any coloration with ferric chloride. [Found: Br, 24·8; Calc. for $C_{12}H_{13}O_5$ Br, Br, 25·2 per cent.]

This acid proved to be *O-5-bromo-2: 4-dimethoxybenoyl propionic acid* as it was also obtained by the bromination of the known *O*-2: 4-dimethoxybenzoyl-propionic acid of Dalal and Nargund. The *Clemmenson reduction*

was carried out as usual and the γ-2 : 4-dihydroxyphyenyl butyric acid crystallised from benzene in small plates, m.p. 105°. [Found: C, 61·0; H, 6·2; $C_{10}H_{12}O_4$ requires C, 61·2; H, 6·1 per cent.]

We take this opportunity of thanking the Principal Rev. Father A. M. Coyne, S.J., and (late) Prof. R. N. Bhagwat, for their kind interest in this work.

Summary

Phthalic anhydride has been condensed with resorcinol with the formation of *O*–2 : 4-dihydroxybenzoyl benzoic acid. Some derivatives of this keto acid have been described.

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A STUDY OF THE CONSTITUENTS OF THE SEEDS OF *CROTON SPARSIFLORUS* (MORUNG)— PART I

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Received July 12, 1941

A—Preliminary Examination of the Seeds

Only two species of the genus *Croton* (family, Euphorbiaceæ), *Croton tiglium* and *Croton elliotianus* [*Meglocarpus* (Hutch)] appear to have been studied in any detail, the former being more thoroughly investigated on account of the physiological activity of the oil. The third member of the genus forms the subject of the present study. The study of this genus is highly interesting since the oils obtained from the seeds of the different species of this genus, vary considerably from one another in their properties.

Apart from a preliminary note by one of us,[2] there appears to have been no chemical investigation of the seed fat of *Croton sparsiflorus*. This plant (*Eliamanakku* and *Naimilakkai* in Tamil and *Kukka Mirapa* in Telugu) is a wild weed, almost becoming a menace to agriculturists and gardeners in South India. It appears to have spread from Bengal where the plant has been imported from South America about the year 1895. Mayuranathan[11] gives a detailed description of the plant. The leaves, the latex and the oil to some extent seem to be used locally as a dermaticide. The whole plant has been reported[1] to contain sufficient potash and nitrogen to be useful when composted as green manure.

The seeds are small and shiny and resemble castor beans. The ripening and the dispersal of the seeds normally take about 10–15 days. The seeds are so small that in the investigation the kernels are not separated, the whole seed being crushed before extraction. On an average a hundred seeds sun-dried for a week, weigh about 0·73 g. and analyse as in Table I.

On extraction successively with several solvents in a Soxhlet, the different amounts were as in Table II.

TABLE I

Analysis of the Whole Sun-dried Seeds

	%
Moisture	8·03
Solvent extractables	38·44
Cake (by difference)	53·53

TABLE II

Solvent	% on sun-dried seeds
Petroleum ether (50–60° C.)	32·67
Ether	1·37
Chloroform	1·19
Ethlyacetate	2·19
Alcohol	1·02

The petroleum ether extract gave a clear yellow oil, practically tasteless with a not disagreeble odour (the carbon tetrachloride extract in the earlier work seems to have given a different result). The oil visibly thickens on exposure to atmosphere and a drying time of 120 hours compares favourably with about 95 hours for raw linseed oil (Calcutta) and suggests its use as a drying oil.

The ether extract resulted in what appears to be three constituents, a white crystalline solid, a colourless amorphous body with a fibrous look and a brown oily liquid. The extract has a strong 'amylic' odour and was irritating to the mucous membrane.

The chloroform extract gave besides the amorphous substance obtained with ether, a darker brown oil somewhat greenish by reflected light. The irritating odour of this extract was characteristic and the substance re-dissolved in chloroform only with difficulty. Fractional precipitation with petroleum ether separated a dirty green amorphous powder, the filtrate from which left a fibrous looking product that could be recrystallised from dioxane to a high melting solid. This has not yet been further investigated.

Extraction with ethylacetate gave a waxy solid that did not re-dissolve in the solvent.

The final extraction with ethyl alcohol gave a dark viscous product which answered the common tests for alkaloids. The Prollius fluid extract also gave positive tests with alkaloidal reagents.

The neutral water extract showed evolution of carbon dioxide and frothing on warming. The extract did not answer tests for reducing substances. Steam distillation of the seeds gave no volatile products.

The analysis of the 'cake' left after the petroleum ether extraction of the oily constituents indicates a very high fibre content and a good percentage of proteins.

The ash content of the seeds was 3·62% and analysed as in Table IV. The high percentage of phosphorus, calcium, sodium and potassium in the ash and sufficiency of nitrogen in the ' cake ' suggests the utility of the meal as manure.

The meal from the oil extracted sample was tested for the hydrolysis of olive oil which established the presence of a lipolytic enzyme in the ' cake '. A qualitative comparison with the castor bean meal which is known to contain a lipase in a very active form showed that the lipase present in this seed is not as active as that in the castor bean.

TABLE III

Analysis of the ' Cake '

	%
Nitrogen (Kjeldahl)	4·97
Proteins (calculated)	31·05
Fibre	37·5

TABLE IV

Analysis of the Ash of the Seeds

	%
Iron as Fe_2O_3	Trace
Calcium as CaO	21·43
Sodium as Na_2O	16·70
Potassium as K_2O	14·33
Phosphorus as P_2O_5	29·88
Silica	13·88
Carbonate (by difference) ..	3·78

B—The Physical and Chemical Constants of the Oil

As indicated in the previous section, the seeds contain a high proportion of fixed oil most of which can be extracted with petroleum ether. The physical and chemical constants of this oil have been determined by usual methods and are collected in Tables V, VI and VII.

TABLE V

Physical Constants of the Oil

Colour (visual)	Light yellow
Odour	Resembles linseed oil
Specific gravity: $d_4^{30.5}$ ..	0·9270
Refractive Index (Abbe):	
$n_{29.5}$	1·4753
$n_{40.0}$	1·4709
Viscosity (in millipoises) ..	28·85

TABLE VI

Chemical Constants of the Oil

Acid Value	9·18
Saponification Value	189·5
Do. (in an atmosphere of nitrogen) ..	190·3
Saponification equivalent (calculated)	295·4
Ester Value (calculated) ..	180·72
% Glycerine	9·88
Acetyl Value	0·02
Iodine Value (Rosenmund-Kuhnhenn) (see also Table VII) ..	163·4
Thiocyanogen-Iodine Value ..	90·41
Hehner Value	91·96
Hexabromide Value (Steele and Washburn)	10·99
Reichert-Meissl Value	1·10
Polenske Value	4·18
Percentage unsaponifiable matter (Kerr-Sorber)	1·36
Do. (continuous extraction) ..	0·98
Maleic anhydride Value ..	3·3
Drying time of film	about 120 hours

TABLE VII

Iodine Value of the Oil by different methods

Method	Reagent	Value
Wijs	Iodine monochloride	172·0
Winkler	Sodium bromide, sodium bromate and hydrochloric acid	168·1
Hanus	Iodine monobromide	163·1
Kaufmann	Alcoholic bromine (with sodium bromide)	163·9
Rosenmund-Kuhnhenn ..	Pyridine sulphate-dibromide	163·4

The high iodine value comparable with that of raw linseed oil indicates a possible use of this oil as a substitute.

Hexabromide values have been usually determined by two methods but tropical temperatures preclude the adoption of the Eibner and Muggan-thaler method that involves filtration of ether solutions. This method did not yield in our hands pure hexabromo-stearic acid and also gave a very high value. Lewkowitsch[9] also considers that the results obtained by this method are unaccountably high. The method of Steele and Washburn[13] has therefore been adopted for the determination of this value.

The Kerr-Sorber method modified by Jamieson and co-workers[7a] for the determination of the unsaponifiable matter in oils involves the ether extraction of a dilute solution of the soap in a separatory funnel. The extraction of appreciable amounts of soap on account of the high laboratory temperature and the formation of stubborn emulsions render this method tedious and of doubtful value. Knapp[8] has shown that this method does not give an accurate estimate of the unsaponifiable matter and that the use of a continuous extractor in the determination has numerous advantages besides a more correct estimation of the percentage of unsaponifiables. The extractor used in the present study, following that designed by Kutsher and Steudd, was similar to that described by Knapp with this modification that the solvent distributor had a flat glass spiral on it, thus ensuring greater circulation of the soap solution. The design of the apparatus allows the maintenance of the extractor at any desired temperature.

The somewhat lower value obtained for the unsaponifiable matter by the continuous extractor method is to be attributed to the complete absence of dissolved soap in the final unsaponifiable matter collected, which is not excluded in the alternative method.

The maleic anhydride value of 3·3 (Ellis and Jones method[6]) may be taken to show the presence of some conjugation. However, it is difficult

to take this as conclusive evidence of any conjugation since it has been shown[4,5] that neither this nor the method of Kaufmann indicate accurately the extent of conjugation in oils of low diene numbers.

The drying time for a thin film of the oil is sufficient indication of the 'drying' properties of the oil. The drying time of 120 hours seems satisfactory for the purpose of a drying oil.

A deep blue colour with arsenophospho-tungstic acid is considered to indicate the presence of linolenic acid in the glyceride in the absence of acids of higher unsaturation.[10] The oil under investigation gave a positive test, though the intensity (visual) is much less than with raw linseed oil.

Experimental

Fully ripe seeds sun-dried for a week were used; and were taken to represent the initial sample in the analysis of seed constituents.

The moisture content was determined by the usual method of drying in an oven at 110° C.

Since the oil polymerises readily, only the sun-dried seeds were used for the determination of solvent extractables, the extraction being carried out in a Soxhlet.

The 'cake' was analysed for the protein, fibre and enzyme content. Nitrogen was estimated by Kjeldahl's method using 0·05 g. selenium as catalyst and 0·5–1·0 g. of cake.

The fibre content was estimated by usual methods.[3] The presence of a lipolytic enzyme was established by the method of Willstätter.[15]

The seeds were ashed at a dull red heat and the several components determined by standard methods of quantitative analysis.

For the determination of the physical and chemical constants of the oil, a petroleum ether extract of the seeds freed from solvent was used. Crushed sun-dried seeds were packed in an extractor of a modified form of Wester's apparatus[14] and the oil extracted with petroleum ether (50–60°). The extract was filtered off from any plant material that might have been mechanically carried through, dried over anhydrous sodium sulphate, and the major portion of the solvent was distilled off. The last traces of solvent were removed under reduced pressure (1–2 mm.). The oil was stored in a brown bottle in an atmosphere of carbon dioxide.

Refractive indices were determined at 29·5° and at 40° using an Abbe refractometer.

Viscosity measurements were made with an Ostwald viscometer, 'conductivity' water and anhydrous, thiophene free, crystallisable benzene of the correct melting point were used for comparison. The measurements were carried out at 30·2°. Taking the viscosity of water as standard from Landolt's tables and using the relation

$$\frac{\eta_1}{\eta_2} = \frac{S_1 t_1}{S_2 t_2}$$

the viscosity of the oil in millipoises was calculated.

Other constants were determined by standard methods.[7] In the determination of the saponification value thymolphthalein was found to be the best indicator both for macro- and semi-micro-determinations of the value.

In the determination of the thiocyanogen-iodine value the reagent was prepared by the method of Gardner and Weinberger. The acetic acid used was the Hopkin and Williams product, purified by the method of Orton and Bradfield.[12] This acid mixed with 10% acetic anhydride ANALAR was used as the solvent. The reagent was stored in a dry amber coloured bottle and tightly stoppered. The reagent was prepared fresh for each estimation. Polymerisation was noticeable on storage.

The method of Knapp[8] was followed in all details in the determination of the unsaponifiable percentage using a continuous extractor. Aliquots from the saponified solution, made up to a definite volume, gave closely comparable values.

The drying test was carried out by usual methods. Raw linseed oil (Calcutta) dried in 95 hours while the oil under investigation dried in 120 hours to the same consistency.

The oil gave a positive test for vitamin A with antimony trichloride.

Summary

The constituents of the seeds of *Croton sparsiflorus* have been examined and the physical and chemical constants of the petroleum ether extractable fixed oil have been determined.

The authors thank the Superintendent, Government Test House, Alipore, for an analysed sample of raw linseed oil that was used for comparison and standardisation of experimental conditions.

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A STUDY OF THE CONSTITUENTS OF THE SEEDS OF *CROTON SPARSIFLORUS* (MORUNG)—PART II

Chemical Examination of the Components

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It has been noticed in Part I that the petroleum ether extract contains most of the solvent extractables and this extract has been used for a more thorough investigation as to the component "resins", unsaponifiables and glycerides.

While the formation of a deep red colour on refluxing with alkali may be indicative of the presence of a resinous component, neither the method of Flaschentrager and Wollffersdorff[6] who isolated the poisonous resinous component or 'Naturstoff' from *Croton tiglium*, nor the more general methods described in text-books gave any appreciable quantity of such a substance in a sufficiently pure state for a complete study. That any such component is present at best in minute amounts only is indicated from the physical and chemical constants of the treated oil which shows no appreciable difference. The method of Cherbuliz[2] also gave a similar result.

The colour with alkali is presumably due to the colouring matter in the seed coat.

As may be expected, the oil contains unsaponifiable matter which could be separated into several components which are still under investigation. A sterol, m.p. 138°, $(\alpha)_{5460.7}^{29.5°C}$. $(C = 0{\cdot}8013) = 56{\cdot}27$ has been isolated. Microscopic examination of the sterol, melting point of the sterol and of the acetyl derivative and the rotation indicate this to be a phytosterol largely consisting of α-sitosterol.

Component Acids.—The chemical examination of the fat may be considered under two heads, the nature of the glycerides and the component acids in the glyceride. Information regarding the latter can be obtained in several ways, and the components definitely established are given in Table I.

TABLE I

Distribution of component acids in the oil (by weight %)

Component acids	Total % in oil	Component acids	Total% in oil
Palmitic	5·49	Linolenic	9·36
Stearic	4·75	Unsaponifiable matter	0·98
Oleic	5·72	Glycerine (by difference) ..	8·02
Δ9:12-octa-decadienoic ..	65·70		

The Hehner value indicates 91·96% of acids saturated and unsaturated together with unsaponifiable matter in the oil. These components were obtained after saponification under standardised conditions (*vide* experimental part). The separation of solid and liquid components has been effected by Twitchell's lead salt alcohol method,[30] some modification, of the same[10] and by direct crystallization from acetone solution.[25] The results of these different methods are appended in Table III.

Mention should be made here of the relative accuracy of the different methods. Repeated trials have shown that Bertram's oxidation method gives accurate results for saturated acids provided the conditions of temperature are maintained so as to completely eliminate hydroxy acids arising from the unsaturated acids (see also Gay[7] and Hilditch and Priestman.[12])

The modified lead salt-alcohol method[10] has been consistently found to yield more accurate results and a purer solid acid than other methods involving lead salts. Rigid control of temperature at 15–16° C. for twelve hours is absolutely necessary for concordant results.

As the methods of separation do not completely eliminate liquid acids, a correction factor based on the iodine value of the two fractions[16] has to be used for an accurate estimation of solid acids.

With reactive unsaturated compounds and with possibilities of isomerization catalysed by the saponifying reagents, lead salt methods are liable to lead to some uncertainty arising from the greater or different solubilities of some of the lead salts. Physical methods of separation are preferable and in the present case, crystallization of the scids in acetone solution at different temperatures have been adopted.

It will be noticed that the component acids are mostly liquid (90%) and these have a high iodine value (Tables II and III).

TABLE II

Method	Reference	Weight % in acids				Weight % in oil*	
		Solid acids			Liquid acids (by difference)	Solid acids	Liquid acids
		Found %	Iodine value	Corrected %			
Twitchell lead salt alcohol ..	(30)	10·92	15·54	9·92	90·08	9·03	81·95
Modified Twitchell lead salt alcohol	(10)	10·85	6·30	10·45	89·55	9·51	81·47
Baugman-Jamieson lead salt ether	(16)	16·78§	30·20	13·80	86·20	12·55	78·43
Bertram oxidation (modified)	(16)	11·25‡	..	11·25	88·75	10·24	80·74
Crystallization method ..	(25)	10·90	..	..	..	9·92	81·06

* Calculated for 90·98% of total acids (Hehner value—unsaponifiable %) in oil from corrected values.

§ Calculated from the value 15·27, obtained for per cent. of saturated acid, direct from oil.

‡ Calculated from the value 10·24 for per cent. of saturated acid, direct from fat.

TABLE III

Details of analysis	Total acid	'Solid' acid	'Liquid' acid (by difference)
Weight % on total acids	100	11·25	88·75
Iodine value (Rosenmund-Kuhnhenn) ..	165·7	0·1	169·5
Thiocyanogen value	91·34	..	92·12
Mean molecular weight	289·3	265·5	1233*

* The high molecular weight of the liquid acids may be due to polymerisation by intermolecular addition of the unsaturated acids.

The solid acids obtained are essentially palmitic and stearic acids. Partial separation of the acids was effected by fractional distillation of the methyl esters under reduced pressure, the rich fractions being used for the preparation and identification of the pure acids. The final estimate of the relative proportions were made by the method of thermal analysis and molecular weight determination.

In establishing the relative amounts of the different unsaturated acids present, bromination, partial oxidation, fractional distillation of methyl esters and Kaufmann's method using thiocyanogen-iodine and iodine values have been employed.

The formation of an ether insoluble crystalline hexabromostearic acid (m.p. 182° C.) while indicative of the presence of linolenic acid in the oil cannot always be taken to be quantitatively representative of the triolefinic acid content (Rollet,[23] Erdman and Bedford[5] and McCutcheon[22]). The low hexabromide value combined with the high iodine value indicates a high proportion of linoleic acid with smaller amounts of oleic and linolenic acids. However, bromination of the mixed fatty acids failed to yield any solid tetrabromide characteristic of α-linoleic acid usually found in seed fats. The high bromine content (50·29%) of the oily liquid from the separation of the hexabromide indicates the presence of a peculiar C_{18}-diethenoid acid. This is considered in greater detail in a later section.

Controlled oxidation of the acids may also be expected to give an insight into the component acids. The method of Lapworth and Mottram[20] was found unsatisfactory and that of Hilditch and Jasperson[11] has been adopted. An impure product, m.p. 124–126°, from which only a very small amount of tetrahydroxy-stearic acid (m.p. 172° C.) could be isolated was obtained. After recrystallization only impure dihydroxy-stearic acid could be obtained. This was obtained in a pure state and in sufficient amounts by a slight modification of the process (Experimental). The isolation of this product connotes the presence of oleic acid in the glyceride. No keto-stearic acid was isolable in the process and only small amounts of hexahydroxy acid could be got.

Complete oxidation of the methyl esters of 'liquid' acids in acetone with potassium permanganate (weakly alkaline) gave *n*-hexoic, oxalic and azelaic acids. The formation of these indicate the presence in the original mixture of $\Delta^{9:12}$-linoleic and linolenic acids.

The close boiling points of the methyl esters ruled out the separation of the constituent acids by fractional distillation of the esters under reduced pressure and all attempts failed to separate the constituents.

It has been found[18] since Kaufmann's thiocyanogen-iodine number determination that a combination of this with iodine values can be used for computing the proportions of the unsaturated acids. If a mixture contains S% saturated acids, X% linolenic, Y% linoleic and Z% oleic acids then

$$100 \times (\text{iodine value}) = 273{\cdot}7\,X + 181{\cdot}1\,Y + 89{\cdot}9\,Z$$

$$100 \times (\text{thiocyanogen value}) = 182{\cdot}5\,X + 90{\cdot}5\,Y + 89{\cdot}9\,Z$$

$$100 = X + Y + Z + S.$$

If S is determined by any of the usual methods, X, Y and Z can be calculated. The results of such a computation are given below:

TABLE IV

Distribution of Fatty Acids in Mixed Acids

Acids	Kaufmann method (weight %)	Bromination method (weight %)
Saturated (Bertram)	11·14	11·14
Oleic	6·30	.. *
$\Delta^{9:12}$-octa-decadienoic	72·28	.. *
Linolenic	10·28	4·04

* The iodine value of the remaining unsaturated acids after allowing for the observed amounts (4·04) of linolenic acid, corresponding to the hexabromostearic acid isolated, was still in excess of that of linoleic acid. This is, in itself, proof that linolenic acid is not completely separated as insoluble hexabromide. It will also be noted that the bromination method records only 39·25% of the linolenic acid content indicated by thiocyanometric analysis.

Though the accuracy of this method has been questioned,[31] it now appears from the work of Hilditch and co-workers[13, 14] that the method is fairly accurate (see however Smith and Chibnall[26]).

C_{18} Acids.—It is necessary, at this stage, to consider in greater detail the C_{18} acids, especially the unsaturated acids.

The formation of hexabromostearic acid (m.p. 182°) by bromination and of dihydroxy stearic acid (m.p. 131°) by controlled oxidation clearly indicate the presence of linolenic and oleic acids in the oil. The evidence for an octa-decadienoic acid is however, not so direct. According to Hilditch[13] (see also foot-note to Table IV) the hexabromide value of an oil measures approximately 40% of the actual linolenic acid present and on this basis, the hexabromide value (10·99) corresponds to 10·1% linolenic acid in the mixture of acids from the oil. If the rest of the mixture were to contain only oleic acid (78·76) and saturated (11·14% observed value) acids, the iodine value of the total acids should be 99·26 while the actual value obtained is 165·7. This clearly indicates a higher unsaturation, than one double bond (if remaining unsaturated acid is diolefinic iodine value should be 170·3). The absence of a benzene insoluble bromide (*vide* Experimental) precludes the presence of higher unsaturation than a trieth-enoid type. One must necessarily conclude that a diethenoid compound is present in appreciable amounts to account for the high iodine value. Further, complete oxidation of the methyl esters leads to *n*-hexoic acid, oxalic acid (presumably from malonic acid) and azelaic acid, clearly pointing to the presence of $\Delta^{9:12}$-octa-decadienoic acid (*vide* Haworth[9]).

The presence of mono-, di- and tri-ethenoid C_{18} acids having been established, it is clear that the thiocyanometric method is the best for

estimating the relative proportions. This gives the values tabulated earlier (Table V). It is significant that with such a high percentage of $\Delta^{9:12}$-octadecadienoic acid, bromination of the unsaturated acid fails to give the petroleum ether insoluble, crystalline tetrabromide (m.p. 114°) characteristic of the common or α linoleic acid but yields an oily liquid bromide soluble in petroleum ether (Bromine content 50·28%). Prolonged keeping of the oily bromide gives a small amount of a low melting waxy solid. It must be mentioned that Kass and Burr[17] have obtained a similar waxy solid (m.p. 75·5–78°) from the products of bromination of elaidinised α linoleic acid. The linoleic acid present in the oil under investigation must therefore be an isomeric form. Our observations, however, are enough to show that this is not likely to be either the *cis-cis* or the *trans-trans* forms.

Evidence for conjugated unsaturation is inadequate but the small but definite maleic anhydride value and effect of weight of sample on the iodine value by Wijs and Hanus methods suggest some conjugation.

The configuration of the linoleic acid is under investigation.

Glyceride structure.—The oil does not contain any fully saturated glyceride, the small quantity of solid resulting from acetone permanganate oxidation being only the unsaponifiable matter.

A preliminary study of the mixed unsaturated saturated glycerides has been made by the fractional crystallization of the brominated glycerides and comparing them with those prepared from linseed oil. The glycerides from linseed oil were separated by the method of Tom.[29] The bromoglyceride corresponding to α-linoleo-di-α-linolenic glyceride melted even after several recrystallisations only at 153° C. Another fraction having m.p. 143° was also isolable. Following Eibner[3] this has been taken to be β-linoleo-di-α-linolenic bromoglyceride.

Following Tom's procedure, the oil under study gave 17·8% of the more insoluble glyceride showing the presence of linoleo-di-linolenic glyceride in the oil. The product had a m.p. 143–144° and the m.p. was not depressed by admixture with a similar product from linseed oil. This must therefore be β-linoleo-di-α-linolenic bromoglyceride. The separation by Suzuki and Yokoyama[28] of two isomeric linoleo-di-linolenin from linseed oil, however, leaves this an open question and further investigation is necessary before establishing the identity of this compound. The absence of a product of m.p. 156° corresponding to the α-linoleic-di-α linolenin indicates that α-linoleic acid is not present in the oil to any appreciable extent.

Another fraction isolated having m.p. 118° probably corresponds to triolein or oleic-linoleic-linolenic glyceride.

It is interesting to compare here the different properties of the three members of this genus.

TABLE V

Comparative Data of the Three Species of the Genus Croton

Characteristics	*Croton tiglium*	*Croton Elliotianus*	*Croton sparsiflorus*
Physiological	A powerful vesicant an irritating purgative	Non-vesicant non-irritating purgative	Non-vesicant no purgative action
Colour	Dark yellow	Yellow	Light yellow
Type of oil	Non-drying	Drying	Drying
% Yields of oil on seeds ..	50	30	32
Iodine value	102–108	143–147·5	164–171

TABLE V—*Contd.*

Component Fatty Acids (Weight %)

Acids	*Croton tiglium*	*Croton Elliotianus*	*Croton sparsiflorus*
Palmitic	1·30*	10·0§	5·97
Stearic	0·50		5·17
Oleic	55·80	10·0	6·30
Linoleic	28·80	80·0	72·28‡
Other unsaturated acids ..	Traces of steam volatile lower acids	..	Linolenic 10·28
Observers	Flaschentrager and Wollffersdorff[6]	Imperial Institute[1a]	Present work

* Also 11·3% myristic and 2·3% arachidic acids.

§ Chiefly palmitic.

‡ The acid is an isomer of usual seed fat linoleic acid.

The constituent acids conform to the general observation that the Euphorbiaceæ seed fats contain about 10% saturated and about 80% unsaturated acids but *Croton tiglium* differs from the other two in the nature of the saturated acids. The oil under investigation is also exceptional in containing linolenic acid and no steam volatile components.

Experimental

Preparation of acids.—The best procedure after several trials was found to be the following: 100 parts of the oil were refluxed on a steam-bath for four hours with a solution of 40 parts of potassium hydroxide in 500 parts of 95% alcohol (by weight). Most of the alcohol was removed by distillation in a current of carbon dioxide, the soaps dissolved in a large volume of water and the unsaponifiable matter removed in a continuous extractor. The

free acids were obtained from this either by acidulation and extraction or by the method of Steele and Washburn,[27] the operations being carried out in an inert atmosphere. Completion of saponification was tested by Geitel's[8] test. For large quantities, the second method works better.

Separation of saturated and unsaturated acids.—The separation of saturated and unsaturated acids was effected by the usual standard lead salt methods and by direct crystallization. The apparatus for this last process can be constructed from common laboratory materials, namely a wide mouthed vacuum jar, a large test-tube and a thistle funnel closed by a filter paper, the arrangement being as in Fig. 1.

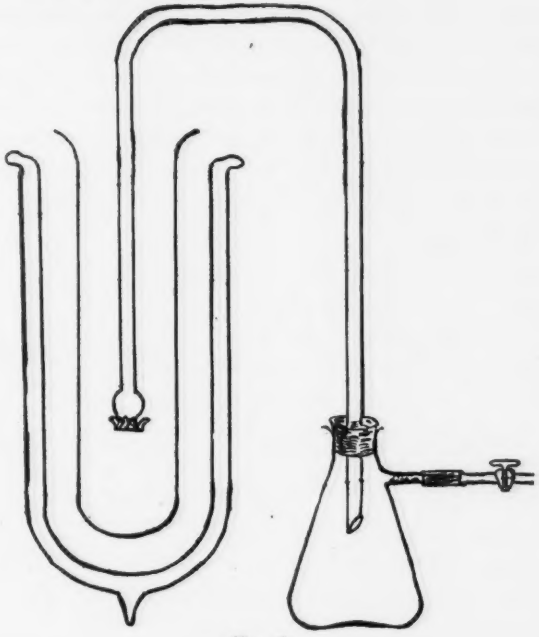

FIG. 1

A solution of the mixed acids in acetone is placed in the test-tube and cooled to different temperatures using appropriate freezing mixtures. After equilibrium at each temperature, the solution was drawn through the filter paper by suction and the residual solid washed with cooled acetone two or three times. The solids thus obtained at each stage indicated a good separation of the components. The advantage of this arrangement over that of Shinowara and co-workers[25] is that all filtrations and washing are carried out at specified low temperatures at which crystallization takes place.

Separation of saturated acids is complete in six hours at $-19°$ to $-22°$ C. From 60 gm. of the total acids 6·54 g. saturated acid were obtained. The same acids were also obtained by Bertram's oxidation method modified by Jamieson[16] correction for adsorbed unsaturated acids being applied by means of the iodine value. Molecular weights of the acids were determined by the usual methods.

Unsaturated acids.—85·73 g. of freshly separated 'liquid' acids (Twitchell's method) were converted into the methyl esters by the usual methods and when purified 73·25 g. of the mixed esters was obtained. 62·5 g. of this mixture was taken in an ordinary Ladenburg flask and distilled under 1 mm. pressure, using a Perkin triangle to collect the fractions. The middle bulb of the flask was two-thirds filled with glass beads supported on a thin strip of copper gauze. The three bulbs and neck were thickly coated with asbestos with slit windows for observation in order to minimise overcondensation of esters. The bottom bulb was completely immersed in an oil-bath whose temperature was maintained 50–60° higher than that indicated by the thermometer at the top of the column. The results of this fractionation are given in the table below.

TABLE VI

Fractional Distillation of the Methyl Esters of the 'Liquid' Acids
(62·47 g.)

No.	Weight in g.	Temperature at head of the column °C.	Iodine value*	No.	Weight in g.	Temperature at head of the column °C.	Iodine value*
1	1·25	140–150§	93·6	5	7·87	158–160	154·0
2	10·95	150–154	129·4	6	14·43	160–162	169·4
3	6·84	154–156	133·7	7	12·88	Residue	..
4	8·25	156–158	148·3				

* Rosenmund-Kuhnhenn method.

§ A few drops collected below 140° C.

All the fractions gave Martins colour test for linolenic acid.[21]

The liquid acid mixture was brominated in chloroform, ether and petroleum ether by adding excess bromine in solution and removing the excess with amylene. In each case after one or two recrystallizations pure hexabromostearic acid, m.p. 181–82° C. was obtained; the identity was established by comparison with an authentic specimen and by analysis. (Br found: 63·6; $C_{18}H_{30}O_2Br_6$ requires Br = 63·3%.) From the residual solutions, no tetrabromostearic acid was isolable in any of the experiments. Prolonged keeping of a petroleum ether solution at or below 0° C. gave rise to a low melting white solid with a bromine content of 50·29%.

Oxidation of liquid acid esters.—The middle fractions from the fractionation of the methyl esters were submitted to oxidation by Haworth's method[9] using potassium permanganate in acetone solution. After oxidation, acetone was distilled off and the residue extracted with a hot dilute solution of sodium hydroxide. The combined extracts were concentrated to 150 c.c. acidified with hydrochloric acid and ether extracted.

The presence of oxalic acid in the aqueous layer was detected by the formation of calcium oxalate, decolourization of potassium permanganate and the formation of urea oxalate. The urea oxalate was compared with an authentic specimen.

The ether extract was washed free of acid, the solvent distilled off and the residue steam distilled. The non-volatile residue was decolourised with animal charcoal in aqueous solution, filtered and allowed to crystallise. White crystals (m.p. 103°) were obtained. On recrystallization, a pure product (m.p. 105·5°, molecular weight 187·5) was got and was identified as azelaic acid.

The volatile distillate was thrice extracted with petroleum ether (50°–60°), dried over anhydrous sodium sulphate and the solvent carefully distilled off. *n*-Hexoic acid was obtained (m.p. Ca −2°) and confirmed by the formation of an anilide (m.p. 92°) (m.p. of *n*-hexoic acid − 2°; m.p. of its anilide 95°).

Partial oxidation of liquid acids by Lapworth's method gave only dihydroxy stearic acid as a product. Dioxane was found to be the best solvent for recrystallizing this compound. (Found: m.p. 131°; mol. wt. 316·2.)

The method of Hilditch and Jasperson[11] gave better results. After oxidation with cold very dilute permanganate, the solution was decolourized with sulphur dioxide and acidified with hydrochloric acid. The precipitated crude hydroxy acid was refluxed with petroleum ether (50–60°) after drying at 65–70° C. to remove unoxidized acids. The residue after filtration was refluxed thrice with ethyl acetate (for 0·77 g. of the crude hydroxy acid, 50 c.c. of the ethyl acetate was used each time) and filtered hot. A small quantity of a white substance was left undissolved and on recrystallization from alcohol melted at 169° (one of the tetrahydroxy stearic acids melts at 172°–73° C.).

The ethyl acetate solution on cooling deposited white crystals (m.p. 124–26°) and further purification did not affect the melting point (mixed m.p. with pure dihydroxy stearic acid 128°). Equivalent weight of this compound was 241·8.

Selective oxidation.—The procedure was based on that of Kaufmann and Fiedler for oleic acid.[10] Mixed acids (14·75 g.) were just made alkaline

with alcoholic potassium hydroxide, diluted to two litres with water, cooled to 0° C. and oxidized with two litres of a 1% solution of potassium permanganate with efficient stirring during 30 minutes. The solution was allowed to stand for 10 minutes, acidified with sulphuric acid and decolourized with sodium bisulphite. The solid obtained was collected on the filter, the solution being examined for hexahydroxy acids.

The crude hydroxy acid (0·91 g.) was taken up with a large volume of warm ether. A very small quantity (0·08 g.) of a brownish substance gave on recrystallizations from alcohol a pure white product melting sharply at 172°. This is presumed to be tetrahydroxy stearic acid.

The ether extract gave a white solid which after washing with petroleum ether gave a powdery substance (m.p. 129°; equivalent weight 334·2). Recrystallization from dioxane gave pearl-white flakes (m.p. 130°) confirmed as dihydroxystearic acid by comparison with an authentic specimen.

The filtrate from the original oxidised solution after separation of the crude hydroxy acid was concentrated to small bulk and acidified. The product after recrystallizations from alcohol and water was very small in quantity (m.p. 196°). Being more soluble in water than the tetrahydroxy acid and with a m.p. higher than that of the known tetrahydroxy acids, this is presumed to be hexahydroxy stearic acid. The quantity obtained was too small for definite identification.

Solid acids.—The solid acids from Twitchell's method were converted into neutral methyl esters and distilled under reduced pressure. The results of fractionation are tabulated below.

TABLE VII

Fractionation of Methyl Esters of 'Solid' Acids

Fraction No.	Temperature at head of the column °C.	Weight of fraction g.	Saponification value	Molecular weight	Acids identified
a	145–54	0·62	204·2	274·9	Palmitic
b	154–57	2·55	203·8	275·4	Palmitic and stearic in small amounts
c	157–60	2·61	203·5	275·7	Palmitic and stearic
d	160–62	1·63	198·2	283·1	Stearic and palmitic
e	162-64	2·23	192·1	292·1	Stearic and palmitic in small amounts
f	163–64	2·14	192·2	292·0	Do.
g	Residue including loss	0·96	192·0	292·2	..

TABLE VIII

Calculated Distribution of 'Solid' Acids

Fraction No.	Palmitic acid (weight in g.) calculated from ester	Stearic acid (weight in g.) calculated from ester	Total acid (weight in g.)
a	0·49	0·10	0·59
b	2.00	0·44	2·44
c	2·00	0·48	2·48
d	0·84	0·70	1·54
e	0·47	1·60	2·07
f	0·47	1·57	2·04
g	0·20	0·71	0·91
Total (weight in g.) ..	6·47	5·60	12·07
% (weight) on solid acids	53·58	46·42	100
Calculated on 11·25% of mixed acids	% (weight) 6·03	5·22	11·25
	% (mole) 6·34	4·91	11·25

Pure palmitic and stearic acids were obtained from the fractions.

Unsaponifiable matter.—The crude unsaponifiable matter was again saponined for one hour. Tne white flakes that separated out on cooling were filtered off and washed with methanol. The product answered the usual colour reactions for sterols. The Rosenheim reaction was negative indicating the absence of conjugation. The sterol was purified by precipitating as the digitonide and decomposing it with pyridine (Schonheimer and Dam[24]). The specific rotation of the sterol was observed in chloroform solution.

TABLE IX

The Constants of the Sterol

Melting point	138° C.
Melting point of acetyl derivative	125° C.
Melting point of digitonide	Softens 206° C.; melts to brown liquid 235° C.
$(\alpha)^{29°.5}_{5460.7}$ (C = 0·8013)	−56·27
$(\alpha)^{29°.5}_{5790.7}$ (C = 0·8013)	−32·64

Small quantities of an alcohol and a low melting solid hydrocarbon were isolated from the filtrate from sterol digitonides but the quantities were inadequate for complete investigations.

Glyceride structure.—Fully saturated glycerides were determined by the oxidation method of Hilditch and Lea.[15]

Reference substances for Tom's method[29] were prepared from pure linseed oil.

The oil under investigation (1 g.) was brominated in ethyl acetate (10 c.c.) at about 0° C. by slow addition of 1 c.c. bromine with efficient stirring. The crude bromoglyceride was separated by filtration, washed with 20 c.c. portions of ethyl acetate and dried at 80°. Further purification with alcohol, ether and tetralin gave a white substance (m.p. 143°) identical with β-linoleo-di-α-linolenin obtained from linseed oil. From the ethyl acetate filtrate a second product unidentified (m.p. 117° C.) was obtained.

The authors thank the Superintendent, Government Test House, for a sample of tested raw linseed oil which was used for comparison.

Summary

The oil from the seeds of *Croton sparsiflorus* has been examined for its composition. Apart from palmeitic, stearic, oleic and linolenic acids, the glyceride contains an unusual isomeric form of the common α-linoleic acid. Complete analysis of the oil has been effected by using Bertram's oxidation method and Kaufmann's thiocyanometric method. Fully saturated glycerides are absent and the oil contains β-linoleo-di-α-linolenin.

The sterol in the unsaponifiable matter is essentially sitosterol.

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CHEMOTHERAPY OF BACTERIAL INFECTIONS

Part V. Synthesis of 2-N^1-Sulphanilamido-5-alkyl- and 2-N^1-Sulphanilamido-4-methyl-5-alkyl-thiazoles

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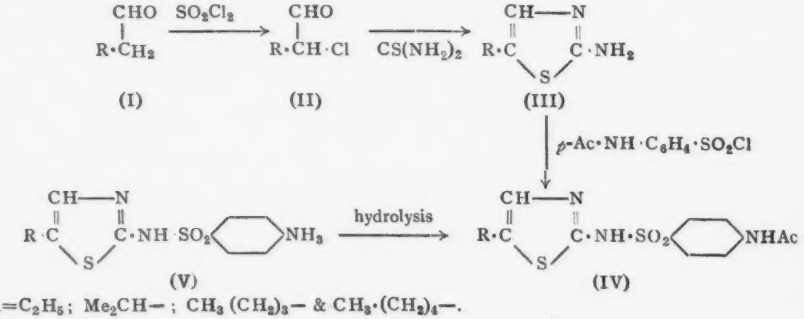
The studies carried out in this Institute on the therapeutic properties of a pilot series of N^1-sulphanilamido derivatives of various ring compounds in experimental *β-hemolytic streptococcal*, (type I) *pneumococcal* and *P. pestis* infections in mice, have led to the discovery of the outstanding therapeutic properties of 2-N^1-sulphanilamido derivatives of thiazole and pyrimidine. The clinical studies carried out hitherto, extensively with the former and to a limited extent with the latter drug, have fully confirmed the results of the animal experiments. As a sequal to this, we undertook to investigate whether, by the proper manipulation of the molecular structure of these drugs, other derivatives could not be discovered which may be more effective or therapeutically active in the treatment of those infections in which they are of little value. The synthesis of many possible types of such compounds was therefore undertaken to study systematically the effects (pharmacological and physico-chemical) of different types of additional substituents in the sulphanilamido derivatives of thiazole and pyrimidine. This paper is concerned with the synthesis of a particular series of 2-N^1-sulphanilamidothiazole derivatives with alkyl substituents in the positions 4 and/or 5 of thiazole; the other types of thiazole and pyrimidine compounds are being reported in the succeeding parts.

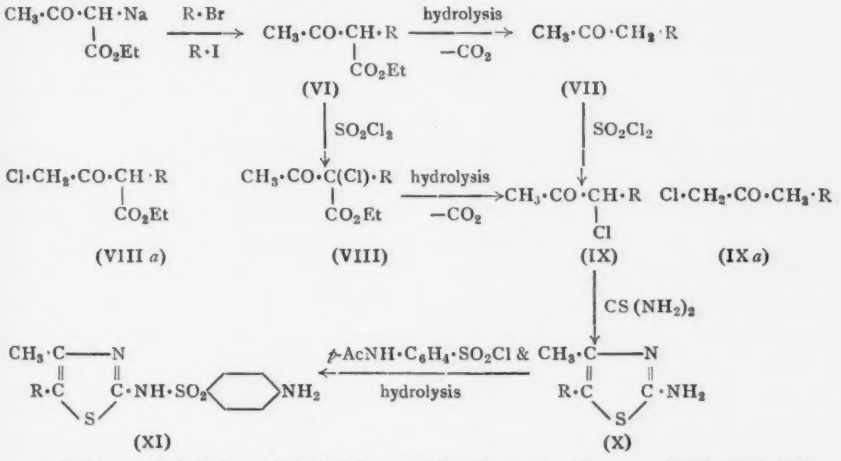
2-N^1-sulphanilamido-5-alkylthiazoles were synthesised according to the following scheme:



R=C_2H_5; Me_2CH-; $CH_3(CH_2)_3-$ & $CH_3\cdot(CH_2)_4-$.

The literature regarding the halogenation of the aliphatic aldehydes (I) is very scanty. Of the 2-amino-5-alkylthiazoles (III), only the 5-methyl derivative has previously been described.[1] It has now been found that the 2-amino-5-alkylthiazoles (III) can smoothly be prepared by chlorinating the alkyl aldehydes (I) with sulphurylchloride and condensing the resulting chloroaldehydes (II) with thiourea. The bromination of the aldehydes was also tried but it appeared to be less advantageous for our purpose since tarry products were formed on condensing the bromoaldehydes with thiourea. The conversion of the aminothiazoles (III) into 2-N[1]-sulphanilamido-5-alkylthiazoles (V) by the usual method was effected in good yields.

The general method adopted to synthesise 2-N[1]-sulphanilamido-4-methyl-5-alkylthiazoles was as follows:—



R=C_2H_5—; $CH_3(CH_2)_2$—; $(CH_3)_2CH$—; $CH_3(CH_2)_3$—; $CH_3(CH_2)_4$—; $(CH_3)_2CH\cdot(CH_2)_2$— & $CH_3(CH_2)_5$—.

In the above scheme, excepting the ketonic esters (VI), ketones (VII) and 3-chloro-2-pentanone, all other compounds are not described in the literature. The preparation of the chloroketones (IX) *via* the chloroesters (VIII) furnished purer products (though in poorer yields) evidently because, the chlorination of the ketonic esters (VI) with sulphurylchloride, as is described,[2, 3] leads exclusively to the chloroketonic esters of formula (VIII), uncontaminated with the isomeric esters of formula (VIII *a*). In the chlorination of the ketones (VII) also with sulphurylchloride, it has been suggested[3] that the chlorine atom enters the methylene carbon atom adjacent to the keto-group with the formation of the chloroketones of formula (IX). We have actually found that the final sulphanilamidothiazoles (XI) obtained

by both the methods are identical. The compounds obtained by the former procedure immediately yielded crystalline products; but those got by the latter did not crystallise readily which is probably due to the contamination of the chloroketone with isomeric products formed during the chlorination of the ketone. The aminothiazoles (X) in a few cases were also prepared *via* the bromoketones; the final sulphanilamidothiazoles obtained from these were also identical with those obtained by the other methods. Since it is known that in the bromination of the ketones (VII) and ketonic esters (VI) the orientation of the bromine atom depends upon the conditions of the reaction, other conditions are being studied to prepare the bromo-compounds corresponding to the chloro analogues (VIII *a* and IX *a*), with a view to preparing from them 2-amino-4-alkylthiazoles.

Since our immediate interest is only the preparation of the sulphanilamidothiazoles (V and XI) and our stock of chemicals is also very limited, the intermediate new products could not be studied in detail at present but will be done at a later date.

The compounds obtained by the above methods are listed in the table. It may be mentioned that 2-sulphanilamido-5-methylthiazole and 2-sulphanilamido-4: 5-dimethylthiazole have been described in a patent of Messrs. May and Baker.[4] The sulphanilamido-alkyl-thiazoles are being tested in many bacterial infections and the results obtained will be reported in due course. If the results are encouraging, further synthesis of more compounds of these groups with higher alkyl groups will be undertaken.

Experimental

2-*N*^{1}-*Sulphanilamido-5-alkylthiazoles* (V):—Since all the compounds were prepared by essentially the same method with but slight alterations in conditions to suit the individual cases, only the general methods are here described.

The aliphatic aldehyde (I) (obtained from the Eastman Kodak Co., Rochester), under external cooling with ice cold water, was gradually treated with 1·1 molecular equivalent of sulphurylchloride. The reaction took place just at about the room temperature (25°–28° C.) and when it tended to become vigorous, the mixture was cooled in ice-cold water. After allowing it to stand with frequent shaking for 2–3 hours, it was poured into cold water, the heavy oil separated, washed free from acid with water and boiled with one molecular equivalent of an aqueous solution of thiourea. The boiling was continued till no more of the oil went into solution (usually 2–5 hours). The solution was then thoroughly extracted with ether to remove

any unchanged material and the aqueous clear solution basified with sodium hydroxide when the aminothiazole separated as an oil. This was taken up in ether, the extract dried and the solvent removed; 2-amino-5-alkylthiazole (III) was thus obtained as a mass of crystals in the case of the butyl and amyl derivatives and as a thick syrup in the rest. Without any further purifications, they were condensed with *p*-acetaminobenzenesulphochloride in pyridine medium to yield the acetyl derivatives of formula (IV) which were then hydrolysed smoothly

TABLE

Serial No.	Name of Compound	Melting Point °C.	Molecular Formula	% NITROGEN	
				Found	Required
	2-Amino-5-amylthiazole	72–73	$C_8H_{14}N_2S$	16·1	16·5
	2-Amino-4-methyl-5-*iso*amylthiazole ..	78	$C_9H_{16}N_2S$	15·2	15·2
	2-N^1-Sulphanilamido-				
87	,, 5-ethylthiazole	170	$C_{11}H_{13}N_3O_2S_2$	14·8	14·8
90	,, 5-*iso*propylthiazole ..	217–18	$C_{12}H_{15}N_3O_2S_2$	14·1	14·1
88	,, 5-*n*-butylthiazole	246	$C_{13}H_{17}N_3O_2S_2$	14·0	13·5
89	,, 5-*n*-amylthiazole	237	$C_{14}H_{19}N_3O_2S_2$	12·6	12·9
80	,, 4-methyl-5-ethylthiazole	193–94	$C_{12}H_{15}N_3O_2S_2$	14·4	14·1
73	,, 4-methyl-5-propylthiazole ..	197–98	$C_{13}H_{17}N_3O_2S_2$	14·0	13·5
78	,, 4-methyl-5-*iso*propylthiazole		$C_{13}H_{17}N_3O_2S_2$	13·0	13·5
72	,, 4-methyl-5-*n*-butylthiazole..	192–93	$C_{14}H_{19}N_3O_2S_2$	13·5	12·9
74	,, 4-methyl-5-*n*-amylthiazole ..	187–88	$C_{15}H_{21}N_3O_2S_2$	12·3	12·4
75	,, 4-methyl-5-*iso*amylthiazole	202–04	$C_{15}H_{21}N_3O_2S_2$	12·2	12·4
79	,, 4-methyl-5-*n*-hexylthiazole..	191–92	$C_{16}H_{23}N_3O_2S_2$	11·9	11·9
	2-N^1-Acetsulphanilamido- ..				
87 Ac	,, 5-ethylthiazole	241–42	$C_{13}H_{15}N_3O_3S_2$	13·4	13·0
90 Ac	,, 5-*iso*propylthiazole ..	200–01	$C_{14}H_{17}N_3O_3S_2$	12·2	12·4
88 Ac	,, 5-*n*-butylthiazole ..	211–12	$C_{15}H_{19}N_3O_3S_2$	11·9	11·9
89 Ac	,, 5-*n*-amylthiazole	229	$C_{16}H_{21}N_3O_3S_2$	11·0	11·4
73 Ac	,, 4-methyl-5-*n*-propylthiazole	236–38	$C_{15}H_{19}N_3O_3S_2$	11·8	11·9
72 Ac	,, 4-methyl-5-*n*-butylthiazole	216–18	$C_{16}H_{21}N_3O_3S_2$	11·6	11·4
75 Ac	,, 4-methyl-5-*iso*amylthiazole	234–36	$C_{17}H_{23}N_3O_3S_2$	11·3	11·0
79 Ac	,, 4-methyl-5-*n*-hexylthiazole..	216–18	$C_{18}H_{25}N_3O_3S_2$	10·8	10·6

to the final 2-sulphanilamido-5-alkylthiazoles (V) with about 4–5 N hydrochloric acid. All the compounds were readily obtained in fine crystalline forms and the overall yields were good in all cases.

2-N^1-*Sulphanilamido*-4-*methyl*-5-*alkylthiazoles* (*XI*).—The general methods of synthesis of these compounds are as follows:—

The alkylbromides (R.Br) used in these experiments were all prepared from the corresponding alcohols by the usual sodium bromide-sulphuric acid method. The condensation of the alkylhalides with sodium ethyl aceto-acetate to yield the alkylketonic esters (VI) and the hydrolysis of these to the

ketones (VII) were carried out according to methods described in Literature. Methylhexylketone was prepared by the oxidation of capryl alcohol.

Method 1.—The methylalkylketone (VII), cooled in ice-cold water, was treated gradually with about one molecular equivalent of sulphurylchloride. The mixture was allowed to stand for about two hours or more with frequent shaking, treated with water, the heavy oil that separated was washed with water, dried and fractionated. The first fraction consisted of the unchanged ketone and the higher boiling one was the required chloroketone (IX) which usually collected within a range of 5–10° C. (this was not refractionated unless the range was much greater). The chloroketone, thus obtained in yields of 80–90%, was boiled with an aqueous solution of thiourea (one molecular equivalent) till no more of the oil could go into solution (2–4 hours). The cooled solution was thoroughly extracted with ether and the clear acid solution basified with sodium hydroxide. The precipitated thick oil was extracted with ether, the extract dried and the solvent removed whereby the aminothiazole (X) was obtained as a syrup (yield, 50–80%). Without any further purification, this was condensed with *p*-acetaminobenzenesulphochloride in pyridine medium. After allowing the mixture to stand overnight it was warmed on the water-bath for about an hour and on dilution with water, a gummy product was obtained which solidified on vigorous scratching (yield, 50–80%). Further purification of this was effected by dissolving it in ammonia or soda solution (charcoal) and precipitating with hydrochloric acid. The 2-acetsulphanilamido-4-methyl-5-alkylthiazole thus obtained was repeatedly crystallised from *iso*propyl alcohol. To prepare the 2-sulphanilamido-4-methyl-5-alkylthiazole (XI), the crude acetyl compound was boiled with about ten parts of 4–5 N hydrochloric acid till the solid went into solution (20–60 minutes). In case the hydrochloride separated on cooling, just enough water was added to get a clear solution. After treating it with charcoal, the partly decolourised solution was neutralised when the final product separated as a gum and solidified on scratching (yield, 60–80%). After a few crystallisations from isopropyl alcohol, the 2-sulphanilamido-4-methyl-5-alkylthiazoles (XI) were obtained as colourless or almost colourless crystals. Only the *iso*propyl derivative, 78, could not so far be obtained as a sharp melting product though it gave the correct analytical figures. According to this procedure, all the compounds except 80 were prepared.

Method 2.—The ketoester (VI) was chlorinated as usual with sulphurylchloride and the resulting chloroester (VIII), obtained in 40–60% yield, was refluxed with a mixture of four parts of 35% sulphuric acid and four

parts of glacial acetic acid for 6–8 hours. The oil obtained on dilution was taken up in ether, the ether extract dried, the solvent removed and the resulting oil fractionated. The chloroketone (IX) thus furnished in yields of 10–40% corresponded in boiling point to that obtained by the previous method. The rest of the procedure in obtaining the final sulphanilamidothiazoles (XI) was as described under method 1. The products obtained by this method were much purer and crystallised very readily. The sulphanilamidothiazoles (XI) obtained by this and the previous method 1 were identical (there being no depression in melting point). According to this method all compounds excepting compounds 74 and 78 were prepared.

Method 3.—The ketone (VII) dissolved in five times the weight of glacial acetic acid and a few drops of hydrobromic acid (48%), under cooling in ice-water, was treated gradually with one molecular equivalent of bromine dissolved in three times the quantity of glacial acetic acid. The decolourisation was immediate and after allowing to stand for about 15 minutes, the solution was poured into cold water, the heavy oil separated, washed free from acid and boiled with one molecular equivalent of thiourea in aqueous solution. The rest of the procedure was as indicated in the previous method 1. According to this method, compounds 72, 73, 74 and 75 were prepared and were found to be identical with the corresponding ones prepared by the foregoing methods.

We express our grateful thanks to Lt.-Col. S. S. Sokhey, Director, Haffkine Institute, Bombay, for his keen interest in these investigations.

Summary

In the course of the attempts to study the effects of the different types of substituents in the molecule of 2-N^1-sulphanilamidothiazole, the synthesis of a series of 2-N^1-sulphanilamido-5-alkyl- and 2-N^1-sulphanilamido-4-methyl-5-alkyl- thiazoles, wherein the alkyl group varies from ethyl to hexyl, have been effected and these compounds are described.

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MODIFIED METHODS FOR THE DETERMINATION OF TOTAL ALKALI, SULPHATE, NITRATE AND PHOSPHATE IN HIGHLY COLOURED SOLUTIONS OF HIGH ORGANIC MATTER CONTENT

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Introduction

During the course of investigations on the waste water from factories like, the textile mills, tanneries, dairies and other industrial concerns considerable difficulty was met with for their analysis, owing to the presence of large proportions of suspended as well as dissolved organic matter, and also due to colour of the solution. These effluents in general are highly coloured—the colour ranging from deep black to deep pink. In such cases the routine methods of quantitative determination of the radicles present in the water are not suitable. The volumetric and colorimetric estimations are rendered impossible owing to the high turbidity and the natural colour of the solutions. In the gravimetric analysis, the precipitates are rendered colloidal due to the peptising action of the dissolved organic matter, thus filtration of the precipitates is made difficult. Furthermore, the precipitates adsorb the colour present in the solutions, and thus account for higher results. This difficulty is more prominent in the case of the determination of sulphate. Thus it is clear that solution under examination should be rendered free from colour, and organic matter, so that routine methods for the analysis of such waters may be employed. With this view several ways of destroying the colour as well as the organic matter present in solutions, in order to render the subsequent analysis of the solution easy, were tried and the results obtained are presented in this paper.

Fowler, in his section on "Water and Water Examinations" in the *Technical Methods of Analysis* by Lunge and Keane has referred to the analysis of sulphates and chlorides present in coloured solutions. He[1] suggests that prior to the estimation of sulphates, the organic matter present in the liquid may be destroyed by boiling with 5–10 drops of fuming hydrochloric acid and a few c.c. of strong chlorine-water. The excess of chlorine is boiled

off, the resulting solution cooled and sulphate determined in the usual way. In the same section, Fowler[2] recommends the use of potassium permanganate for the destruction of colour and organic matter present in the solutions prior to the analysis of chlorides. But it will be seen that these methods are not of universal application.

In a previous communication by the author[3] it has been shown that hydrogen peroxide may be used with advantage to oxidise the organic matter in order to render the solution colourless, prior to the analysis of chlorides by the usual silver nitrate titration method. The excess of hydrogen peroxide which is left unused is boiled off with a little alkali, and the chloride determined in the usual way. Quite concordant and reliable results have been obtained by this modification of the method. This new procedure has now been extended to the analysis of several of the radicles present in highly coloured and turbid waters, and the details of the methods in each case have been worked out. The results obtained in all the above cases have been presented in the following pages.

Experimental

(*A*) *Determination of total alkali.*—For the volumetric determination of the total alkali by the indicator method, it is necessary that the solution under examination should be absolutely colourless; and free from suspended as well as dissolved organic matter. Fowler's methods (*loc. cit.*) of rendering the solution clear and colourless are unsuitable in these cases since either of his procedures would interfere with the radicles present in the water. The hydrogen peroxide method on the other hand, has been found to be quite useful, and the experimental procedure is as described below:

A known volume (50 c.c.) of the filtered liquid is transferred into a 250 c.c. conical flask and heated to boiling. Then 10 per cent. hydrogen peroxide (Merck A. R. redistilled quality free from acids, etc.) is added from a burette drop by drop until a faint colouration remains. The contents of the flask are then boiled until the colour gets completely discharged and the evolution of oxygen ceases. The liquid is then cooled, and quickly filtered through paper, all washings being done with freshly boiled distilled water. The resulting colourless and clear solution is titrated against standard acid with methyl orange as indicator and the total alkalinity of the sample is determined. The results are calculated as parts of sodium carbonate per 100,000.

Also, parallel determinations were made on solutions of known alkalinity. The results obtained are quite concordant as shown by the following table:

TABLE I

Analysis of Total Alkalinity

(*Parts per* 100,000)

No.	Source of the sample	Description of the sample	Total alkalinity expressed as parts of sodium carbonate per 100,000	
1	*Textile Trade Waste Water*—			
	(*a*) Sample I Dye-house waste ..	Highly turbid; coloured green	133·55	
	(*b*) Sample II ,, ..	Turbid; coloured black	67·74	
	(*c*) Sample III Mixed waste ..	Turbid; coloured brown	66·42	
2	*Tannery Waste Water*—			
	(*a*) Sample I	Coloured pale yellow	Trace	
	(*b*) Sample II	Viscous; pale yellow	2·6	
3	Sample of water from a local tank full of dispersed organic matter	Coloured pale green and highly turbid	3·8	
4	*Standard Solutions*—			
	(*a*) 80 parts of NaOH *plus* 53 parts of Na_2CO_3	Clear and colourless	Sodium hydroxide 79·3	Sodium carbonate 54·0
	(*b*) 40 parts of NaOH *plus* 53 parts of Na_2CO_3	,,	39·1	53·4

(*B*) *Sulphate.*—The estimation of sulphate in trade wastes was carried out by the method described by Treadwell and Hall.[5] Prior to the determination of the sulphate, the trade waste samples were decolourised by the two methods: (1) The Fowler's chlorine-water method and (2) the hydrogen peroxide method described below.

A known volume of the filtered sample of the liquid (100 c.c.) is pipetted into a conical flask and heated to boiling. Then a few c.c.'s of 10 p.c. hydrogen peroxide are added drop by drop until the colour of the solution is almost discharged. The contents of the flask are then boiled for a few more minutes to decompose the excess of hydrogen peroxide. If necessary a few drops of strong sodium hyroxide solution are added to hasten the decomposition of the peroxide. The liquid is then filtered and the sulphate in the filtered liquid determined by precipitating it as barium sulphate.

The same procedure is followed in the determination of the other radicles described in the paper.

The results obtained are presented in Table II.

Parallel determinations of sulphate were carried out with solutions of known sulphate content with a view to test the accuracy of the methods employed. The results of these analysis are also included in Table II.

An examination of Table II shows that the hydrogen peroxide method gives results which are quite reliable and agree with those got by the Fowler's method.

TABLE II

Sulphate

(*Parts per* 100,000)

No.	Source of the sample	Description of the sample	Hydrogen peroxide method (Author)	Chlorine-water method (Fowler)
1	*Textile Trade Waste Water*—			
	(*a*) Sample I Dye-house waste ..	Highly turbid; greenish	40·3	40·1
	(*b*) Sample II ,, ..	Turbid; coloured black	22·6	22·85
	(*c*) Sample III Mixed waste ..	Turbid; coloured brown	36·45	36·0
2	*Tannery Waste Water*	Viscous; pale yellow	11·66	12·48
3	*Dairy Waste Water*	Opalescent	7·40	7·70
4	*Sample of water from a local tank* ..	Coloured green and plenty of suspended matter	3·12	3·20
5	*Standard Potassium Sulphate solution*			
	(*a*) Containing 126·6 parts of SO_4'' soln.	Clear and colourless	126·0	125·6
	(*b*) ,, 63·3 parts of SO_4'' soln.	,,	63·05	63·0
	(*c*) ,, 31·56 parts of SO_4'' soln.	,,	31·20	31·35

(*C*) *Nitrate.*—The proportion of nitrate present in such effluents is not usually high and hence only colorimetric methods are suitable for its determination. As in previous cases the effluents are to be made colourless and clear, before estimation of the nitrates are conducted, as otherwise the original colour of the solutions makes the analysis impossible. A comparative study of Fowler's chlorine-water method and the hydrogen peroxide method (for decolourisation) has been made. The nitrate has been estimated by the phenol disulphonic acid method.[6] The results are presented in Table III. As before, parallel determinations of nitrate have been made with solutions of known nitrate content and the results are included in Table III.

An examination of Table III shows that the hydrogen peroxide method gives reliable and accurate results. It may also be pointed out that the Fowler's chlorine-water method is elaborate as it invariably involves the precipitation of the chlorides with silver sulphate. The removal of the chlorides is necessary since they interfere in the phenol disulphonic method for the determination of nitrates.

TABLE III

Nitrate Nitrogen

(*Parts per* 100,000)

No.	Source of the sample	Description of the sample	Hydrogen peroxide metho s (Author)	Chlorine-water method (Fowler)
1	*Textile Trade Waste Water—*			
	(*a*) Sample I Dye-house waste ..	Highly turbid; greenish	16·6	15·8
	(*b*) Sample II „	Turbid; coloured black	21·1	20·2
	(*c*) Sample III „ ..	Turbid; coloured brown	7·15	7·01
2	*Tannery Waste Water—*			
	(*a*) Sample I	Coloured pale-yellow; viscous	3·02	3·00
	(*b*) Sample II	„	2·8	2·55
3	*Dairy Waste Water—* Sample I	Faintly greenish; highly turbid	0·62	0·60
4	Local tank water containing large quantity of dispersed organic matter	Greenish and turbid	0·86	0·89
5	*Standard Solution—*			
	(*a*) Containing nitrate nitrogen 10 parts per 100,000	Colourless and clear	9·80	9·82
	(*b*) Containing nitrate nitrogen 5 parts per 100,000	„	4·82	4·76

(*D*) *Phosphate.*—The proportions of phosphate present in the effluents under examination have been so low that only the colorimetric methods are suitable for their determination, and the Denige's method modified by Florentin and Atkins[7] has been found to be quite suitable.

The hydrogen peroxide method for the destruction of colour and organic matter of the solution has been employed. But in this case it is quite necessary that the resulting solution after boiling with hydrogen peroxide should be absolutely free from hydrogen peroxide, as otherwise erroneous results and often negative tests for phosphates are obtained. Thus the resulting solution after filtration is again boiled for sometime with a few drops of phosphate-free alkali, and when the hydrogen peroxide has been completely

decomposed, the solution is cooled, and made upto a known volume and the phosphate determined by the modified Danige's method. The method consists in matching the blue colour produced by the addition of 2 c.c. of molybdic acid solution and 0·5 c.c. of stannous chloride solution to the sample of water under test, with similar solutions of known phosphate content. The results obtained are accurate and the reliability of the method has been found out as before by carrying out a series of determinations with solutions of known phosphate content. The results are as shown in Table IV.

TABLE IV

Phosphate

(*Parts per* 100,000)

No.	Source of the sample	Description of the sample	Hydrogen peroxide method (Author)
1	*Textile Trade Waste Water*—		
	(*a*) Sample I Dye-house waste	Highly turbid; greenish	1·62
	(*b*) Sample II „	Turbid; coloured black	1·25
	(*c*) Sample III Mixed waste	Turbid; coloured brown	1·36
2	*Tannery Waste Water*—		
	(*a*) Sample I	Coloured pale yellow and viscous	6·65
	(*b*) Sample II	„	5·02
3	*Dairy Waste Water*	Faintly greenish and turbid	2·03
4	*Sample of Tank Water*	Greenish and turbid	0·018
5	*Standard Sodium Phosphate Solution*—		
	(*a*) Containing 5 parts of PO_4''	Clear and colourless	4·82
	(*b*) Containing 2 parts of PO_4''	„	1·91
	(*c*) Containing 1·5 parts of PO_4''	„	1·32

Conclusion

As shown in the foregoing pages the analysis of highly coloured and turbid effluents has been much simplified by the previous oxidation of colour and organic matter by hydrogen peroxide under suitable conditions. It has also been shown that the hydrogen peroxide method is more convenient than the other two methods, namely the permanganate method and the chlorine-water method. The hydrogen peroxide method can moreover be

employed for determination of total alkali, whereas the other two methods are unsuitable.

It must however be conceded that the bicarbonate, the nitrite and sulphite, escape determination by any of the above methods since all of them are decomposed during the pre-treatment of the effluents under analysis. While the bicarbonates get precipitated as their carbonates during the course of pretreatment and thus are removed out of the solution during the subsequent filtrations, nitrite and sulphite are oxidised to nitrate and sulphate respectively, thus adding to proportions of nitrate and sulphate already present. Further work on this aspect of the problem is in progress.

The estimation of stable radicles in turbid and highly coloured fluids can be conveniently conducted after the pretreatment with hydrogen peroxide. It may be confidently hoped that this method will find a wide application in the biological analysis of highly coloured liquids of biological origin.

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THE COLOURING MATTER OF THE FLOWERS OF *TAGETES PATULA*: ISOLATION OF A NEW FLAVONOL, PATULETIN AND ITS CONSTITUTION

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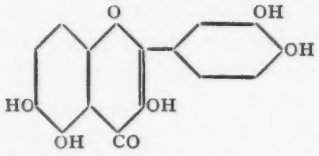
Tagetes patula, the French Marigold (called *Seemabanthi* in Telugu) is similar to *Tagetes erecta*, except that it has a bushy and spreading habit. The flowers are much smaller in size, but borne in larger numbers. In colour they are red tinted and variegated. They do not seem to have been investigated before. It has been recently pointed out by us[1] how De La Source and Perkin on the one hand and Mahal on the other, thought that they were dealing with the two different species, but actually examined one and the same species *Tagetes erecta*. The confusion arose from a wrong combination of the botanical and the common names.

A genuine sample of the flowers of the *patula* was collected and examined according to the general method already outlined in some of our past publications.[2] The concentrated alcoholic extract of the petals did not deposit any solid even after several days but on dilution with water, a pale yellow crystalline substance separated out in good yield. After the removal of this solid, the mother-liquor was successively treated with neutral and basic lead acetate solutions, when an orange-red precipitate was produced in each case. The aqueous solution obtained by the decomposition of the neutral lead acetate precipitate did not yield any solid even after six months. It, however, contained a glucoside and on hydrolysis produced glucose and an aglucone which was found to be identical with the yellow substance obtained by the dilution of the original alcoholic concentrate. The glucoside itself could not be obtained and experiments are being carried out to effect its isolation. The basic lead acetate fraction was not much and was therefore, discarded.

The pale yellow crystalline solid isolated as given above is found to be a new pigment, and is named " Patuletin ", as it has been obtained from the flowers of the *patula*. It has the elementary formula $C_{15}H_{10}O_7$ and melts at 262–64°. On treatment with lead acetate it gives a deep red precipitate, and in 50% alkali it undergoes ready oxidation in the cold, thereby indicating that it is a flavonol. The substance yields a pentaacetyl derivative and a pentamethyl ether, and hence it should be a tetrahydroxy flavonol. It is, therefore, isomeric with quercetin and herbacetin. As a result of oxidation in alkaline solution, it yields protocatechuic acid, which could be isolated

after methylation, in the form of veratric acid. So the flavonol contains two hydroxyl groups in the 3′ and 4′ positions. Since the naturally occurring hydroxy flavones and flavonols with the exception of one or two invariably contain a hydroxyl group in position 5, it is very likely that the new substance does not add yet another member to the exceptions to the general rule, and hence it may be presumed that one of the two hydroxyl groups in the benzopyrone ring is in position 5. For the other hydroxyl therefore, one of the remaining three positions 6, 7 and 8 is available. It does not seem to be present in position 8, as the substance is not oxidised by *p*-benzoquinone to give the " gossypetone " reaction (*cf.* cannabiscetin[3]). Nor can it be in position 7, as the compound is not identical with quercetin. Hence patuletin is tentatively represented as 3: 5: 6: 3′: 4′-pentahydroxy flavone.



In further support of the above structure, it may be pointed out that the flavonol present in the closely allied species *T. erecta* has two hydroxyl groups in 5 and 6 positions (quercetagetin). The resemblance between patuletin and quercetagetin is very close in regard to many of their reactions. Like the latter the new flavonol immediately dissolves in alkali forming yellow solutions. When treated with a drop of ferric chloride, an alcoholic solution of the substance produces a greenish brown colour. With alkaline buffer solutions, as in the case of quercetagetin, no prominent colour changes are produced. When treated with sodium amalgam (Bargellini's test), patuletin immediately yields bluish green flocks; but the colour changes to almost pale yellow in about ten minutes and remains so even after 48 hours. By the action of diazomethane, the pigment undergoes complete methylation. This may be counted as evidence against the existence of a hydroxyl group in the 5th position. But the objection cannot be valid since quercetagetin itself is completely methylated under the same conditions.[4] The resistance of the hydroxyl group in position 5 to methylation seems to be dependent on the disposition of other hydroxyls in the ring and to be greatest when they are present in the 5–7–8 combination as in herbacetin[5] and gossypetin.[6]

Support for the suggested structure of patuletin is expected to be obtained from synthesis which is in progress.

Experimental

Isolation of Patuletin.—The dry petals (1,000 g.) of the flowers of *Tagetes patula* were extracted twice with boiling alcohol, each extraction

lasting over 12 hours, and the extract concentrated to about 300 c.c. After filtering through fluted filters the resins and the waxes that separated out, the clear concentrate was allowed to stand for a month; but no solid was deposited. It was, therefore, diluted with a large volume of water (1,500 c.c.), when a yellow crystalline solid began to precipitate out. The next day it was filtered and washed with water. As it was still impure and sticky, it was dissolved in a little pyridine and water was added to the solution till the impurities separated out as a suspension. They were coagulated by the addition of calcium chloride and filtered off. The clear filtrate which did not develop any more turbidity on further dilution was concentrated till the pigment separated out as yellow needles. Further purification of the substance was effected by crystallisation twice from alcohol, when it came out as clusters of dull yellow needles sintering at 260° and melting at 262–64°. It was sparingly soluble in water but easily dissolved in pyridine, alcohol and acetic acid. (Found in air-dried sample: C, 53·5; H, 4·4; $C_{15}H_{10}O_7$, $2H_2O$ requires C, 53·5; H, 4·1%. Found in the sample dried at 120° *in vacuo*: C, 59·4; H, 3·5; $C_{15}H_{10}O_7$ requires C, 59·6; H, 3·3%.) On acetylation with acetic anhydride and anhydrous sodium acetate, the pigment yielded a pentaacetyl derivative melting at 170–72°. It crystallised from dilute acetic acid as clusters of colourless needles. [Found: C, 58·1; H, 3·9; $C_{15}H_5O_2$ $(OCOCH_3)_5$ requires C, 58·6; H, 3·9%.]

The Neutral Lead Acetate Fraction.—The aqueous solution left after the removal of the new flavonol was treated with excess of neutral lead acetate. The orange red precipitate produced was filtered, washed, suspended in water and decomposed with hydrogen sulphide. The aqueous solution thus obtained was concentrated and left aside after the addition of a few drops of toluene. Even after six months no pigment separated out but a small amount of resin settled down. The clear liquor was extracted with ether and the extract yielded a small amount of patuletin on evaporation. To see if the aqueous solution contained any glucosides, it was made 7% acid by the addition of the calculated amount of concentrated sulphuric acid and boiled under reflux. In about fifteen minutes some brown solid separated giving rise to bumping, and the subsequent heating had to be carried out on a boiling water-bath. After two hours, the contents were cooled and filtered. A portion of the filtrate was neutralised with barium carbonate, concentrated to a small bulk and then treated with phenyl hydrazine in acetic acid solution, when an osazone was produced. This was identified as glucosazone melting at 204–06°. The solid residue was brown in colour and it was contaminated with a considerable amount of resin, which could not be removed by direct crystallisation. So the mixture was macerated with cold alcohol when all the brown resin went into solution leaving most of the pigment

behind. By this treatment and subsequent crystallisation from fresh alcohol, it was obtained as clusters of yellow needles melting at 260–62°. It was identified as the new flavonol, patuletin, from a study of its properties and the comparison of the acetyl derivatives.

Properties of Patuletin.—The substance was not a glycoside since it remained unaffected, when boiled with 7% sulphuric acid for two hours. It very easily dissolved in alkalis producing orange-yellow solutions. Ferric chloride imparted a brownish green colour to an alcoholic solution of the substance. When a small amount of sodium amalgam was added to a solution of the substance in absolute alcohol, bluish green flocks were immediately produced ; but their colour changed to almost pale yellow in about 10 minutes and remained so even after 48 hours. Neutral lead acetate produced a deep red precipitate, when added to an alcoholic solution of the pigment. When a solution of the substance in absolute alcohol was treated with *p*-benzoquinone, the original colour of the solution did not change, nor did any solid separate out even after several days. The colour reactions of the flavonol with alkaline buffer solutions were not prominent. In this and most of the other properties given above, it resembled quercetagetin closely.

Alkaline Oxidation of the Flavonol: Isolation of Veratric Acid.—The flavonol (1 g.) was treated with 50% aqueous potash (20 c.c.) when it dissolved immediately to form an orange-yellow solution. On leaving exposed to air with occasional shaking for 24 hours, the solution became opaque and brown. It was then diluted, and treated with excess of dimethyl sulphate (20 c.c.) in small quantities. After shaking for an hour, the contents were heated on a water-bath for about 30 minutes to complete the methylation and decompose the excess of the dimethyl sulphate. The clear alkaline solution was then acidified, and extracted with ether, when a colourless crystalline acid was obtained. It crystallised from alcohol in the form of needles melting at 183–84° and was found to be identical with veratric acid.

Preparation of Pentamethyl Patuletin.—(*a*) Pentaacetyl patuletin (0·5 g.) was dissolved in acetone (20 c.c.) and treated in small quantities alternately with dimethyl sulphate (10 c.c.) and 20% sodium hydroxide (10 c.c.). Subsequently further quantities of dimethyl sulphate (5 c.c.) and alkali (5 c.c.) were added, and finally the medium was made definitely alkaline by the gradual addition of more alkali (15 c.c.). After leaving overnight, the mixture was refluxed for half an hour to complete the methylation. When the excess of the solvent was distilled off, a yellowish white substance was produced. It was recrystallised from dilute acetic acid using a little animal charcoal, when it appeared as colourless needles and narrow rectangular plates.

(*b*) The flavonol (1 g.) was dissolved in anhydrous methyl alcohol (50 c.c.) and then treated in small quantities during two days with excess of diazomethane (3 g.) in ether solution. After each addition, the mixture assumed an orange colour which gradually faded on subsequent shaking. After the completion of the reaction, the ether and the excess of diazomethane were driven off on a water-bath, when a brown solid was left behind. On crystallisation from alcohol using a little animal charcoal, the ether was obtained as colourless narrow rectangular plates.

The two samples of the ether as obtained by the above methods were found to be identical. The pure substance sintered at about 143° and melted completely at 158–59°. [Found: OCH_3, 39·6; $C_{15}H_5O_2(OCH_3)_5$, H_2O requires OCH_3, 39·7%.]

Alkaline Oxidative Hydrolysis of Pentamethyl Patuletin.—The Pentamethyl ether (1 g.) was refluxed in a silver flask with 50% potash (20 c.c.) for 6 hours, at the end of which it was completely disrupted. The clear alkaline solution on acidification did not precipitate any solid. When extracted with ether, however, and when the ether solution was evaporated, a crystalline solid was obtained and was found to be identical with veratric acid melting at 182–84°.

Summary

A new flavonol, patuletin has been isolated from the petals of the flowers of *Tagetes patula* (French Marigold). It contains five hydroxyl groups and yields a pentaacetate and a pentamethyl ether. It is, therefore, isomeric with quercetin and herbacetin. On oxidation in cold alkali, the substance decomposes into protocatechuic acid which could be isolated after methylation as veratric acid. The completely methylated ether also yields veratric acid on boiling with potash. Assuming that a hydroxyl group is present in position 5, as is the case with most of the naturally occurring flavones and flavonols, the remaining hydroxyl group in the compound is concluded to be in position 6 in view of the properties of the flavonol and its resemblance to quercetagetin. Hence patuletin is represented as 3: 5: 6: 3′: 4′-pentahydroxy flavone.

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FINITE STRAIN IN A ROTATING SHAFT

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The theory of finite strain in elastic problems has been developed on the hypothesis that we do not neglect the second order terms in the components of strain.[1,3] Some applications of it have been given in recent papers.[2,4-9] When applied to the case of a solid rotating shaft we get an exact solution of the stress equations of equilibrium, and the comparison of the results with those given by the small strain theory becomes quite interesting.

We treat the problem as one of plane strain, with an allowance for uniform longitudinal extension, α. Since the shaft is strained symmetrically we can take the components of displacement as

$$u = x(1-\beta),\ v = y(1-\beta),\ w = \alpha z, \tag{1}$$

where β is a function of $r = (x^2+y^2)^{\frac{1}{2}}$ only.

The stress components are given by

$$\widehat{xx} = \lambda\delta + \mu\left[(1-\beta^2) - x^2\left(\beta'^2 + \frac{2\beta\beta'}{r}\right)\right], \tag{2·1}$$

$$\widehat{yy} = \lambda\delta + \mu\left[(1-\beta^2) - y^2\left(\beta'^2 + \frac{2\beta\beta'}{r}\right)\right], \tag{2·2}$$

$$\widehat{zz} = \lambda\delta + \mu(2\alpha - \alpha^2), \tag{2·3}$$

$$\widehat{yz} = \widehat{zx} = 0, \tag{2·4}$$

$$\widehat{xy} = -\mu xy\left(\beta'^2 + \frac{2\beta\beta'}{r}\right), \tag{2·5}$$

where

$$\beta' = d\beta/dr, \text{ and}$$

$$\delta = 1 - \beta^2 - \tfrac{1}{2}(r^2\beta'^2 + 2r\beta\beta') + \alpha - \tfrac{1}{2}\alpha^2. \tag{3}$$

In polar co-ordinates these stresses are given by

$$\widehat{rr} = \lambda\delta + \mu[1-(r\beta'+\beta)^2], \tag{4·1}$$

$$\widehat{\theta\theta} = \lambda\delta + \mu(1-\beta^2), \tag{4·2}$$

$$\widehat{r\theta} = \widehat{rz} = \widehat{\theta z} = 0, \tag{4·3}$$

with $\widehat{zz}$ given by (2·3).

The only stress-equation of equilibrium which is not identically satisfied is given by

$$\frac{\partial \widehat{rr}}{\partial r}+\frac{\partial \widehat{rz}}{\partial z}+\frac{\widehat{rr}-\widehat{\theta\theta}}{r}+\rho\, r\,\omega^2=0, \tag{5·1}$$

which, on substituting from (4), reduces to

$$\frac{\partial}{\partial r}\left[\beta^2+(r\beta'+\beta)^2+c\int r\beta'^2\,dr-\frac{c}{2\mu}\rho r^2\omega^2\right]=0,$$

where

$$c=\frac{2\mu}{\lambda+2\mu}=\frac{1-2\eta}{1-\eta},$$

and ω is the angular velocity of the shaft.

Since η, the Poisson's ratio, lies between 0 and $\frac{1}{2}$, c lies between 0 and 1.

The differential equation statisfied by β is therefore

$$\beta^2+(r\beta'+\beta)^2+c\int r\beta'^2\,dr-\frac{c}{2\mu}\rho r^2\,\omega^2=\mathrm{K}_1, \tag{5·2}$$

K_1 being a constant.

The general solution involving one arbitrary constant can be obtained in the form of an infinite series. In the present paper we propose to discuss only the particular solution obtained from (5·2) by putting $\mathrm{K}_1=0$. This is easily seen to be

$$\beta=\mathrm{A}r=\frac{c\,\rho\,\omega^2\,r}{\mu\,(10+c)}. \tag{6}$$

The radial displacement is therefore given by

$$\mathrm{U}=r\left(1-\frac{c\,\rho\omega^2\,r}{\mu\,(10+c)}\right). \tag{7}$$

The boundary condition over the curved surface is $\widehat{rr}=0$ over $r=a$, being the radius of the shaft in the strained condition. Using (4·1) we get

$$(3-2c)-(1-c)\,(1-\alpha)^2=a^2\mathrm{A}^2\,(5-c). \tag{8}$$

The boundary condition over the plane ends is $\widehat{zz}=0$ over $x=\pm l$, $2l$ being the length of the shaft. This cannot be exactly satisfied. But we can make the resultant longitudinal tension vanish over the plane ends. This requires

$$\int r\widehat{zz}\,dr=0, \tag{9·1}$$

which gives

$$(3-2c)-(1-\alpha)^2=\tfrac{4}{5}\,a^2\,\mathrm{A}^2\,(1-c). \tag{9·2}$$

We have now the three equations (6), (8), (9·2) to determine the two constants A and α. This implies an identical relation between ρ, a and ω. This is the natural consequence of the fact that (6) is only a particular solution, and not the general solution.

The constants α and A are given by

$$(1-\alpha)^2=\frac{(3-2c)(5+3c)}{5+8c-5c^2}, \tag{10·1}$$

$$A^2a^2=\frac{2c(3-2c)}{5+8c-5c^2}, \tag{10·2}$$

and the identical relation is given by

$$\rho a^2\omega^2=\frac{2\mu(3-2c)(10+c)}{5+8c-5c^2}. \tag{10·3}$$

The non-vanishing stresses are now given by

$$\widehat{rr}=\frac{5-c}{10+c}\rho\omega^2(a^2-r^2), \tag{11·1}$$

$$\widehat{\theta\theta}=\frac{\rho\omega^2}{10+c}[a^2(5-c)-r^2(5-4c)], \tag{11·2}$$

$$\widehat{zz}=\frac{5\rho\omega^2(1-c)}{2(10+c)}(a^2-2r^2). \tag{11·3}$$

If $\widehat{rr}_0$, $\widehat{\theta\theta}_0$, $\widehat{zz}_0$, denote the corresponding stresses of the small strain theory, we have[10]

$$\widehat{rr}_0=\tfrac{1}{8}(4-c)\rho\omega^2(a^2-r^2), \tag{12·1}$$

$$\widehat{\theta\theta}_0=\tfrac{1}{8}\rho\omega^2[a^2(4-c)-r^2(4-3c)] \tag{12·2}$$

$$\widehat{zz}_0=\tfrac{1}{4}(1-c)\rho\omega^2(a^2-2r^2). \tag{12·3}$$

If α_0 is the corresponding value of α_1 we have for ω given by (10·3),

$$\alpha_0=-\frac{1}{2}\cdot\frac{(1-c)(10+c)}{5+8c-5c^2}. \tag{13}$$

Instead of making the resultant longitudinal tension vanish we can suppose that the tension is adjusted on the plane ends so that the length is maintained constant. In such a case $\alpha=0$, and the identical relation (10·3) takes the form

$$\rho a^2\omega^2=\frac{\mu(2-c)(10+c)}{c(5-c)}. \tag{14}$$

$\widehat{rr}$, $\widehat{\theta\theta}$ retain the form given in (11), but $\widehat{zz}$ and $\widehat{zz}_0$ become

$$\widehat{zz}=\frac{\rho\omega^2(1-c)}{(2-c)(10+c)}[2(5-c)a^2-5(2-c)r^2], \tag{15·1}$$

$$\widehat{zz}_0=\frac{\rho\omega^2(1-c)}{4(2-c)}[(4-c)a^2-2(2-c)r^2]. \tag{15·2}$$

If U_0 is the radial displacement of the small strain theory, we have[10]

$$U_0 = \frac{\rho\omega^2 r}{16\mu\,(3-2c)}\,[(2-c)\,(1+2c)\,a^2 - c\,(3-2c)\,r^2]. \qquad (16)$$

If r_1 and r_{10} are the values of r for which U and U_0 vanish, we have

$$\frac{r_1}{r_{10}} = \left[\frac{(5+8c-5c^2}{2\,(2-c)\,(1+2c)}\right]^{\frac{1}{2}}. \qquad (17)$$

Since $0 < c < 1$, this ratio lies between 1·118 and 1·155. For $\eta = \frac{1}{4}$ ($c = \frac{2}{5}$), the difference can be as much as 12 per cent.

In like manner we find that (a/a_0) lies betewen 1 and 0·732. For $\eta = \frac{1}{4}$, the difference between the two values is about 10 per cent.

For comparing the stresses we find

$$\frac{\widehat{rr}}{\widehat{rr_0}} = \frac{8\,(5-c)}{(10+c)\,(4-c)}, \qquad (18\cdot1)$$

$$\frac{\widehat{zz}}{\widehat{zz_0}} = \frac{10}{10+c}. \qquad (18\cdot2)$$

The ratio in the first case varies between 1 and 0·97, and in the second case between 1 and 0·91. For the cross-radial stress we find that $(\widehat{\theta\theta}/\widehat{\theta\theta_0})$ lies between 1·2 and 0·97.

It appears that, though the stresses given by the two theories are similar in form, the radial displacements have not the same character. Also, the mistake involved in using the small strain theory can be as much as 10 to 12 per cent.

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DECOMPOSITION OF HYDROGEN PEROXIDE BY SODIUM NITROPRUSSIDE

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Qureshi (1931) pointed out that the decomposition of hydrogen peroxide by sodium nitroprusside in visible light is followed by a marked photochemical after-effect. The reaction in the unilluminated mixture was found to be exceedingly slow, but the decomposition in the pre-illuminated mixture was observed to follow the unimolecular law. He suggested that the after reaction is due to colloidal Prussian blue formed from nitroprusside during irradiation. Preliminary experiments conducted by the present author showed that although the dark decomposition is very slow, the reaction in the pre-insolated mixture is not unimolecular. An attempt was, therefore, made to investigate this after-effect, and to ascertain the nature and the rôle of the catalyst, which is responsible for the non-cessation of the reaction after cutting off the illumination. The photochemical after-effect in H_2O_2-$K_4Fe(CN)_6$ reaction has been shown by the author (1939) to be due to the photo-formation of potassium aquopentacyanoferrite. It was of interest to examine whether the after-effect in the above reaction might also be traced to a similar cause.

In view of the meagre experimental work on this reaction, it was thought desirable to take up an exhaustive investigation of the problem and try to elucidate the chemical mechanism of the after-effect. Experiments have been conducted with:—

(i) pre-insolated H_2O_2-nitroprusside reaction mixture;

(ii) pre-insolated sodium nitroprusside added to hydrogen peroxide in the dark;

(iii) end solutions of pre-insolated H_2O_2-nitroprusside mixtures added to fresh hydrogen peroxide in the dark.

All the experiments were carried out at 35° C. The volume of the reaction mixture was 50 c.c. in all cases, and the strength of hydrogen peroxide was N/10. The velocity constants have been calculated from the usual unimolecular formula, $K = 1/t \log a/a-x$, where 't' is the time in minutes,

and '$a-x$' is the concentration of H_2O_2 in terms of c.c. of $KMnO_4$ at time 't'.

Photochemical After-effect

The dark reaction is negligibly slow. Sodium nitroprusside (0·0200 gm.) dissolved in conductivity water was added to the calculated amount of hydrogen peroxide and the mixture was made up to 100 c.c. It was insolated and when the evolution of oxygen became marked, it was transferred to the dark room. The reaction in this mixture was found to be autocatalytic. It has been observed in connection with another investigation that the decomposition of hydrogen peroxide by sodium aquopentacyanoferrate follows an autocatalytic course, but fairly uniform unimolecular velocity constants are obtained in presence of a suitable excess of potassium ferrocyanide. It was consequently of interest to see if the addition of potassium ferrocyanide to the insolated mixture could give uniform values of the unimolecular constant.

In order to study the effect of potassium ferrocyanide, 100 c.c. of the reaction mixture was insolated as above. It was then divided into 50 c.c. portions and kept in the thermostat. The reaction in the first portion was followed as usual. The other portion of the insolated mixture was treated with the requisite amount of potassium ferrocyanide. The mixture was allowed to stand in the thermostat until all the ferrocyanide had dissolved, and then the decomposition of hydrogen peroxide was followed volumetrically. The amount of permanganate taken up by ferrocyanide was allowed for (by subtraction) from the total volume used in each titration.

TABLE I

Without $K_4Fe(CN)_6$

t	$a-x$	K.10^5
0	13·45	...
23	11·50	296
61	7·70	397

TABLE II

With $K_4Fe(CN)_6 = 0·1320$ *gm.*

t	$a-x$	K.10^4
0	9·20	...
10	6·90	125
15	5·80	134
24	4·50	129
35	3·50	120
54	1·90	127
72	1·10	128

It is evident that in the absence of ferrocyanide, the reaction shows an autocatalytic course and the velocity constants calculated by the unimolecular formula increase with the progress of the reaction. In the presence of an excess of ferrocyanide, however, constants are obtained for the

unimolecular formula. Their absolute values are also much higher than when no ferrocyanide is used.

After-effect with Pre-insolated Nitroprusside added to H_2O_2 in the Dark

Experiments were performed with pre-insolated nitroprusside added to hydrogen peroxide in the dark. Sodium nitroprusside (0·2500 gm.) was made up to 500 c.c. in conductivity water and insolated in bright sunlight, until a pale brownish yellow colour appeared. This did not take more than 7 to 10 minutes. The solution was removed to the dark before any blue tint could be noticed. The volume of this solution used in the following experiments was 20 c.c. (0·0100 gm.). (See Table III.)

The unimolecular velocity constants are seen to increase with time. The effect of ferrocyanide in varying quantities was next investigated and the following results were obtained. The volume of pre-insolated nitroprusside was 20 c.c. in each case.

TABLE III

t	$a-x$	K.10^6
0	15·00	..
60	14·80	97
128	14·60	105
230	14·15	110
310	13·70	127
418	13·15	137

TABLE IV

$K_4Fe(CN)_6 = 0·0060$ *gm.*

t	$a-x$	K.10^6
0	14·35	..
42	13·00	1020
76	12·45	812
108·5	11·95	732
134	11·80	634
210	10·95	559
293	10·05	528
354	9·45	512

TABLE V

$K_4Fe(CN)_6 = 0·0132$ *gm.*

t	$a-x$	K.10^5
0	14·40	..
43	11·70	210
75	10·20	200
99	9·15	199
209	5·65	194
295	4·55	170
356	3·90	159

TABLE VI

$K_4Fe(CN)_6 = 0·0396$ *gm.*

t	$a-x$	K.10^5
0	13·75	..
20	10·25	638
60	6·10	588
83·5	4·30	605
101·5	3·10	637

For the sake of brevity, the other tables are not reproduced, but the results have been summarised below and illustrated in Fig. 1, curve '*a*'.

The after-effect has been calculated by subtracting the dark rate of uninsolated nitroprusside-ferrocyanide-hydrogen peroxide mixture from the rate of pre-insolated nitroprusside-ferrocyanide-hydrogen peroxide mixture.

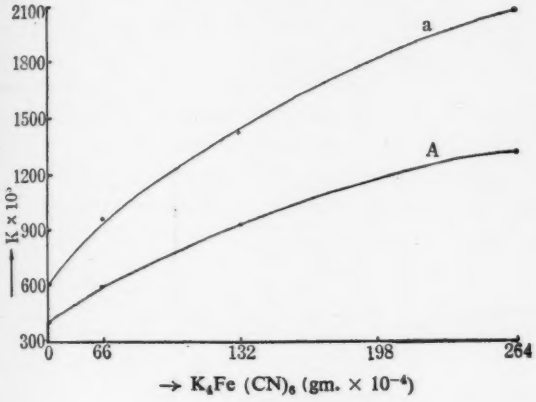

FIG. 1

TABLE VII

$K_4Fe(CN)_6$ used in gm.	After-effect $K.10^5$
0·0060	Decreasing rate
0·0132	do.
0·0396	609
0·0660	957
0·1320	1415
0·2640	2079

The above results show that in presence of an excess of ferrocyanide, not only are uniform values of unimolecular velocity constants obtained, but their absolute values are very much higher than those obtained in experiments in which no ferrocyanide is added. Moreover, the greater the amount of ferrocyanide added, the higher is the velocity constant. When very small amounts of ferrocyanide (0·0060 gm., 0·0132 gm.) are used, the velocity constants show a falling off with time. This result is strikingly similar to that observed in ferrocyanide-hydrogen peroxide reaction from the view-point of the photochemical after-effect. The pre-insolated nitroprusside solution does not show any colour change with dilute sulphuric acid, *p*-nitrosodimethylaniline, or nitrosobenzene. But when ferrocyanide is added to pre-insolated nitroprusside solution containing any of the above reagents, very characteristic colour changes are produced in the dark. The first two reagents give a green colouration while the third reagent, *i.e.*, nitrosobenzene, gives a violet colouration. These tests are not given by uninsolated nitroprusside to which ferrocyanide has been added in the dark.

Effect of Concentration Change on Pre-insolated Nitroprusside with Constant Concentration of Ferrocyanide

The results obtained by employing varying quantities of pre-insolated nitroprusside solution with a constant amount (0·0660 gm.) of ferrocyanide have been summarised below and illustrated in Fig. 2, curve '*b*'. The

details of one experiment, using 1 c.c. of pre-insolated nitroprusside (0·0005 gm.) are given below:

TABLE VIII

Pre-insolated nitroprusside
1 *c.c.* (0·0005 *gm.*)

t	*a*—*x*	K.10⁵
0	14·10	..
22	13·05	153
50	11·80	155
126	9·55	134
154	8·75	135
181	8·10	133
209	7·40	134

TABLE IX

Nitroprusside in gm.	After-effect K.10⁵
0·0005	148
0·0015	279
0·0025	432
0·0050	650
0·0100	957
0·0150	1157
0·0200	1337

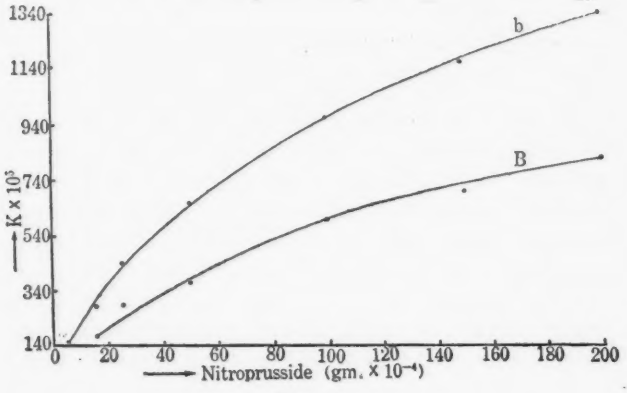

FIG. 2

The concentration of ferrocyanide being kept constant, the velocity constants depend upon the amount of pre-insolated nitroprusside. The greater the concentration of pre-insolated nitroprusside, the higher is the value of the velocity constant. Potassium ferrocyanide has been employed in considerable excess in the above experiments.

The following experiment shows the effect of potassium ferricyanide on the reaction mixture of hydrogen peroxide and pre-insolated nitroprusside. The concentration of ferricyanide was the same as that of ferrocyanide, *i.e.*, M/320, and the amount of pre-insolated nitroprusside was 20 c.c., *i.e.*, 0·0100 gm.

TABLE X

t	$a-x$	K.10^5
0	14·95	..
16	14·60	64
61	13·40	78
121·5	7·00	271
181	1·80	508
211	0·85	590

The effect of ferrocyanide (in increasing and keeping constant) on the unimolecular velocity constants is quite specific, as ferricyanide does not regulate the reaction. The obvious conclusion is that the catalyst, formed from nitroprusside on insolation, is changed to a more reactive substance by interaction with ferrocyanide and is kept at a constant concentration when the latter is used in excess. Potassium ferricyanide does not show this behaviour.

Diminution in the Reactivity of Pre-insolated Nitroprusside

The catalyst formed by insolation of nitroprusside is fairly stable, as by heating the pre-insolated solution to about 90° C. for a few minutes before mixing with hydrogen peroxide-ferrocyanide mixture, the same rate of decomposition is obtained as with the unheated solution. Moreover, a pre-insolated solution of nitroprusside continues to give the same rate of decomposition even many days after insolation. But a very striking change was observed when a mixture of ferrocyanide and pre-insolated nitroprusside was heated to about 90° C. for a few minutes before adding to hydrogen peroxide. The value of the velocity constant (K. 10^6) comes down from 4450 to about 250. It is significant that pre-heated ferrocyanide, when added to pre-insolated nitroprusside, does not show this tremendous diminution in the catalytic activity. It is evident, therefore, that the catalyst obtained by irradiation of nitroprusside is comparatively stable towards heat, but the more reactive substance formed by interaction of pre-insolated nitroprusside and ferrocyanide in the dark is destroyed by heating the mixture to 90° C. This change was also observed when ferrocyanide-pre-insolated nitroprusside mixture was kept in the dark at room temperature (30° C.) for 48 hours before the experiment. The product of interaction between ferrocyanide and the catalyst formed in pre-insolated nitroprusside thus undergoes a slow spontaneous change in the dark with a concomitant diminution in its catalytic activity. The reactivity of pre-insolated nitroprusside in the presence of ferrocyanide is much suppressed by cyanide ions. The after-effect due to the pre-insolated nitroprusside is almost completely ' quenched'

by sodium nitrite also. The strength of potassium cyanide was N/400 and that of sodium nitrite, N/100. Sodium nitrite was added to pre-insolated nitroprusside and ferrocyanide and this mixture was added to hydrogen peroxide. The excess of nitrite had reacted with hydrogen peroxide before the first reading was taken, and consequently no allowance for nitrite in the titrations was necessary. The effect of heat, standing in the dark for 48 hours, cyanide ions and sodium nitrite is recorded in Tables XI, XII, XIII and XIV respectively. The curves A, B and C in Fig. 3 illustrate

TABLE XI

t	K.10^6
0	..
20	261
61	208
108	184
138	176

TABLE XII

t	K.10^6
0	..
25	244
60	205
196	160

TABLE XIII

t	K.10^6
0	..
30	203
120	153
188	148
205	147
310	169

TABLE XIV

t	$a-x$	K.10^6
0	14·60	..
30	14·45	150
60	14·30	152
117	14·10	130
185	13·60	167
255	13·20	172

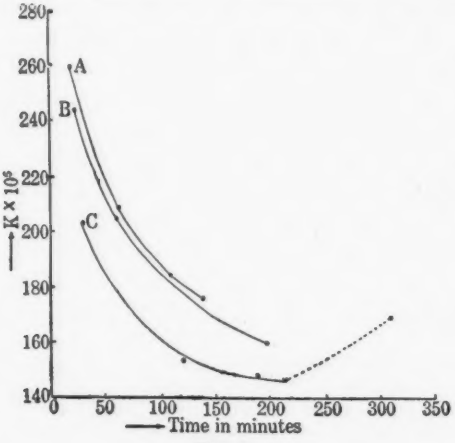

FIG. 3

N.B.—The uninsolated nitroprusside-ferrocyanide mixture gives constant values (K. 10^6=126).

the respective effect of heat, spontaneous change in the dark after 48 hours and lastly of cyanide ions.

The control experiment between uninsolated nitroprusside (0·0025 gm. and ferrocyanide (0·0660 gm.) gave constant values of unimolecular velocity constant, K. $10^6 = 126$. The same value of K is obtained when no nitroprusside is used. When potassium cyanide (N/400) was employed together with the above two reactants in the dark, the course of the reaction became autocatalytic, probably due to the alkali obtained from potassium cyanide by hydrolysis. It is clear that the velocity constants obtained above tend to approach the values obtained in the control.

Secondary After-effect

The effect of adding fresh hydrogen peroxide in the dark to the end solution of pre-insolated nitroprusside-hydrogen peroxide mixture has been called the secondary after-effect (*cf.* MacMahon and Lal, 1940). It has been studied by restoring in the dark the hydrogen peroxide used up in the insolated mixture. A mixture (500 c.c.) of hydrogen peroxide (N/10), and nitroprusside (0·2500 gm.) was prepared and insolated, until the evolution of oxygen became marked. It was then brought back to the dark room, and allowed to stand until all hydrogen peroxide was decomposed. This end solution was taken in measured quantities and the reaction performed by adding fresh hydrogen peroxide to restore the original strength (N/10). (See Table XV.)

The end solution, when added to fresh hydrogen peroxide in the dark, shows an autocatalytic course similar to that observed with pre-insolated nitroprusside. The effect of ferrocyanide in varying amounts was studied on this mixture as well. The amount of the end solution used in each case was 20 c.c. (0·0100 gm.).

TABLE XV

End solution = 20 *c.c.*

t	$a-x$	K.10^6
0	14·70	..
55	14·55	80
116	14·10	156
175	13·70	175
236	12·95	233

TABLE XVI

$K_4Fe\ (CN)_6 = 0·0132$ *gm.*

t	$a-x$	K.10^5
0	14·10	..
13	12·95	284
39	11·90	184
72·5	10·85	157
107	9·80	148
140	8·95	141
176·5	8·20	133
243	7·10	123
278	6·60	119

The other results are summarised below (Table XVIII). The after-effect has been calculated by subtracting from the total rate the dark rate with uninsolated nitroprusside and ferrocyanide in each case.

TABLE XVII

$K_4Fe\,(CN)_6 = 0{\cdot}0396$ *gm.*

t	$a-x$	K.10^5
0	14·10	..
20	11·55	433
40	9·30	454
73	7·20	400
109	5·25	394
142	3·70	409
178	2·30	443

TABLE XVIII

$K_4Fe\,(CN)_6$ in gm.	After-effect K.10^5
0·0132	Decreasing rate
0·0396	414
0·0660	597
0·1320	925
0·2640	1419

These results have been illustrated in Fig. 1, curve 'A'. They show that except when a very small amount of ferrocyanide is used, the velocity constants are uniform and higher than in the experiments in which no ferrocyanide is used to an extent depending upon its concentration.

Variation of the End Solution with Constant Amount of Ferrocyanide

In the following experiments the amount of potassium ferrocyanide was kept constant (0·0660 gm.) and the amount of the end solution was varied. The results have been graphically shown in Fig. 2, curve 'B', and summarised below:

TABLE XIX

Nitroprusside in end solution in gm.	After-effect K.10^5
0·0015	169
0·0025	288
0·0050	366
0·0100	597
0·0150	689
0·0200	815

The results show that for a fixed amount of ferrocyanide the rate of decomposition is higher, the greater the amount of the end solution.

Reproduction of the Photochemical After-effect in the Dark

Previous investigation of the photochemical after-effect in H_2O_2-$K_4Fe\,(CN)_6$ reaction by the author (*loc. cit.*) has shown that the photoformation of potassium aquopentacyanoferrite from aqueous potassium

ferrocyanide causes the phenomenon. It was only natural to suppose that sodium nitroprusside on insolation produces a similar or identical product, which continues to exert its influence even after darkening. It was, therefore, thought desirable to study the decomposition of hydrogen peroxide in presence of sodium aquopentacyanoferrate and uninsolated nitroprusside. Sodium aquopentacyanoferrite was prepared in the laboratory by the method of Hofmann (1900). It was oxidised with hydrogen peroxide, and sodium aquopentacyanoferrate of violet colour was obtained in required amounts.

In the following experiments, 0·0010 gm. of sodium aquopentacyanoferrite was oxidised with hydrogen peroxide. The oxidation was quick, and when all the peroxide had decomposed, the aquopentacyanoferrate so formed was added to uninsolated nitroprusside solution (0·0100 gm.) and hydrogen peroxide, both in presence and absence of potassium ferrocyanide.

TABLE XX

Without ferrocyanide

t	$a-x$	K.10^5
0	14·80	..
12	14·60	49
26	13·60	142
35·5	12·90	168
51	11·45	219
72	8·90	307
115	6·00	341

TABLE XXI

$K_4Fe\,(CN)_6 = 0{\cdot}0660$ *gm.*

t	$a=x$	K. 10^5
0	14·00	..
9	11·80	825
23	8·80	877
34·5	7·25	826
49	5·70	796
66	4·10	808
109	1·50	890

The concentration of sodium aquopentacyanoferrate in the following experiments was 2·5 times the concentration employed above.

With higher concentrations of ferrocyanide, uniform velocity constants were obtained. The following are the results (Table XXIII).

TABLE XXII

$K_4Fe\,(CN)_6 = 0{\cdot}0132$ *gm.*

t	$a-x$	K.10^5
0	14·10	..
10	11·50	885
22·5	9·90	683
35	8·70	599
51·5	7·50	532
78·5	6·00	473
112	4·60	434
149	3·30	423

TABLE XXIII

$K_4Fe\,(CN)_6$ in gm.	K.10^4
0·0396	114
0·0660	135

In the above experiments, aquopentacyanoferrate obtained by oxidation of aquopentacyanoferrite, according to the reaction

$$2\ Na_3Fe(CN)_5 \cdot H_2O + H_2O_2 = 2\ Na_2Fe(CN)_5 \cdot H_2O + 2\ NaOH$$

contains alkali. It was feared that these traces of alkali might react with nitroprusside and vitiate the results. It was, therefore, thought necessary to prepare pure sodium aquopentacyanoferrate, from sodium nitroprusside, caustic soda and bromine according to the method of Hofmann (*loc. cit.*). The blue violet powder so obtained was used with uninsolated nitroprusside and the following results were obtained. The amounts of sodium aquopentacyanoferrate and sodium nitroprusside in 50 c.c. of the reaction mixture were 0·0010 gm. and 0·0100 gm. respectively.

TABLE XXIV

Without ferrocyanide

t	$a-x$	K.10^5
0	9·70	..
40	9·40	34
80	8·30	85
93	7·60	114
108	7·05	128
135	6·10	149

TABLE XXV

$K_4Fe\ (CN)_6 = 0{\cdot}0660$ *gm.*

t	$a-x$	K.10^4
0	9·05	..
7	8·00	76
16	7·10	66
30	6·00	60
51	4·60	58
85	2·90	58
115	1·80	61

TABLE XXVI

Heated ferrate-nitroprusside-ferrocyanide mixture to 90° *C., cooled and added to* H_2O_2 $K_4Fe\ (CN)_6 = 0{\cdot}0660$ *gm.*

t	$a-x$	K.10^4
0	9·10	..
18	8·95	4
55	8·70	4
97	8·00	6
121	7·70	6

It is clear that the reaction with a mixture of aquoferrate and nitroprusside is autocatalytic as already seen in the above experiments. An excess of ferrocyanide regulates the reaction, and gives considerably higher velocity constants. These results show that uninsolated nitroprusside-aquopentacyanoferrate mixture qualitatively reproduces the results obtained with insolated nitroprusside. The effect of heat on the uninsolated nitroprusside-aquopentacyanoferrate mixture containing ferrocyanide is shown

in Table XXVI. Here also, by heating the above mixture to about 90° C. for a few minutes before adding to hydrogen peroxide, a tremendous fall in the velocity of decomposition is observed. The mixture to which ferrocyanide is added after heating does not show any fall in its catalytic activity. Again, the effect of cyanide ions on the uninsolated nitroprusside-aquopentacyanoferrate mixture has been observed to be the same as in the case of pre-insolated nitroprusside, namely, a considerable diminution in the velocity constants. Sodium nitrite, which has been shown to suppress the after-effect almost completely, shows the same retarding effect in this case also. The details are given in Table XXVII. The strength of nitrite was N/100.

Effect of Alkali on H_2O_2-Nitroprusside Dark Reaction

Although the rate of reaction was not measurable in the dark, it was observed that the addition of alkali to the mixture causes a rapid decomposition of hydrogen peroxide, similar to that obtained in pre-insolated nitroprusside-hydrogen peroxide-ferrocyanide mixture. In the following experiment (Table XXVIII), 0·0100 gm. of sodium nitroprusside was used, and the strengths of alkali and hydrogen peroxide were N/200 and N/10 respectively. No ferrocyanide was added.

TABLE XXVII

Treated ferrate-nitroprusside mixture with sodium nitrite and added this mixture to H_2O_2 $NaNO_2 = N/100$

t	$a-x$	K.10^4
0	6·50	..
22	6·40	3
46	6·05	5
88	5·70	6
139	5·15	7
207	4·60	7
242	4·20	8

TABLE XXVIII

t	$a-x$	K.10^5
0	14·80	..
28	12·40	275
55	10·65	260
81	9·20	255
125	7·10	255
186	4·60	273
235	3·10	289

It is well known that traces of alkali render hydrogen peroxide extremely unstable. In order to test the effect of alkali, therefore, a control experiment was performed using ferrocyanide and sodium hydroxide (0·0660 gm., and N/200 respectively). The resulting velocity constants were almost of the same order as without alkali, although the reaction was slightly autocatalytic. It is, therefore, clear that the amount of alkali employed above does not account for a rapid decomposition of hydrogen peroxide, observed in the foregoing experiment. The end solution was deep yellow

and gave an emerald green colour with *p*-nitrosodimethylaniline, and a violet colour with nitrosobenzene, indicating the formation of sodium aquopentacyanoferrite. The effect of potassium cyanide on the above mixture was next investigated to see whether a suppression of the decomposition was produced. Mixtures (50 c.c.) of nitroprusside, caustic potash, hydrogen peroxide, and potassium ferrocyanide were prepared, in which the respective strengths were 0·0100 gm., N/200, N/10 and 0·0660 gm. The strength of KCN was N/50.

TABLE XXIX

Without potassium cyanide

t	$a-x$	K.10^4
0	14·00	..
10	10·40	129
25	6·30	139
38·5	3·70	150
50	2·10	163

TABLE XXX

With potassium cyanide

t	$a-x$	K.10^4
0	13·30	..
5	12·60	47
15	11·60	40
33	9·85	40
64	8·10	34
101	6·90	28
127	6·40	25
160	5·90	22
190	5·60	20

The reaction in presence of ferrocyanide is slightly autocatalytic. When, however, N/50 potassium cyanide is used, a tremendous decrease in the velocity constant is observed and the values show a falling off with time. The explanation is that sodium aquopentacyanoferrite is produced by interaction of alkaline nitroprusside and hydrogen peroxide (Hofmann, *loc. cit.*). The aquopentacynoferrite so formed decomposes hydrogen peroxide at a rapid rate. On the addition of potassium cyanide, the following reaction takes place:—

$$Fe(CN)_5 \cdot H_2O''' + CN' = Fe(CN)_6'''' + H_2O.$$

Aquopentacyanoferrite ions disappear producing ferrocyanide with a concomitant decrease in the velocity constant.

These results are similar to those obtained with pre-insolated nitroprusside-ferrocyanide-cyanide-hydrogen peroxide mixtures, and aquopentacyanoferrate-uninsolated nitroprusside-ferrocyanide-cyanide-hydrogen peroxide mixtures. In view of these observations, the suggestion of Qureshi (*loc. cit.*) that colloidal Prussian blue, formed by insolation, causes the after-effect, seems to be untenable. To examine this point, colloidal Prussian blue was prepared in the laboratory by the method of Hofmann, and added to hydrogen peroxide both in presence and absence of ferrocyanide. The

amount of Prussian blue (0·0025 gm.) was the same as that of aquopentacyanoferrate used before.

TABLE XXXI

Without $K_4Fe\,(CN)_6$

t	$a-x$	K.10^7
0	14·80	..
66	14·70	455
132	14·60	447
194	14·50	464
248	14·45	419

TABLE XXXII

$K_4Fe\,(CN)_6 = 0·0660$ *gm.*

t	$a-x$	K.10^5
0	14·80	..
65	11·80	151
131	10·90	101
191	10·20	85
247	9·60	76

It is clear that colloidal Prussian blue causes a very slow unimolecular decomposition. In the presence of ferrocyanide, the velocity constants, although higher, show a diminution with time—a behaviour different from that of aquopentacyanoferrate-ferrocyanide-hydrogen peroxide mixture, or pre-insolated nitroprusside-ferrocyanide-hydrogen peroxide mixture. It appears, therefore, that colloidal Prussian blue does not cause the after-effect.

The pre-insolated nitroprusside solutions as well as the end solutions of hydrogen peroxide-nitroprusside insolated mixtures developed a turbidity and showed colloidal particles under the ultramicroscope. An aqueous solution of sodium aquopentacyanoferrate also shows colloidal particles. The effect of colloidal ferric hydroxide was insignificant, indicating that it does not cause the observed after-effect.

Discussion

Qureshi's suggestion (*loc. cit.*) that the photochemical after-effect in the above reaction is due to the formation of colloidal Prussian blue has been experimentally found to be untenable. The latter is produced when aqueous nitroprusside is insolated for a long time, but the results set out above lead to the conclusion that it is not responsible for the after-effect. It is necessary to mention here that preliminary experiments showed that the blue nitroprusside solutions obtained by prolonged insolation gave erratic results, although even in these blue solutions the suggested catalyst, sodium aquopentacyanoferrate, could be chemically detected. Satisfactory results were, however, obtained by employing solutions of nitroprusside which had become pale yellowish brown on insolation and in which no blue tint was noticeable. These observations show that in the initial stage of insolation a new substance is formed which causes the after-effect, and longer exposures lead to the formation of colloidal Prussian blue. The results set out above show

that qualitatively the behaviour of pre-insolated nitroprusside, the pre-insolated mixture of hydrogen peroxide and nitroprusside, and the end solution of pre-insolated mixture of hydrogen peroxide and nitroprusside is identical with that of sodium aquopentacyanoferrate and nitroprusside mixture in the dark.

A reference to the literature on the action of light on nitroprusside shows that the formation of colloidal Prussian blue has been taken to be the result of insolation. According to Overbeck, sodium nitroprusside decomposes slowly in sunlight, yielding NO and $Fe_7(CN)_{18}$. The latter corresponds to Prussian blue, $Fe_4^{III}(Fe^{II}CN_6)_3$'. On the other hand, Justin-Mueller (1935) says that when exposed to sunlight in an open vessel, an aqueous solution of sodium nitroprusside is decomposed giving $NaNO_2$, HCN and $Na_2Fe_2(CN)_6$. The last named, in the presence of caustic soda, is converted into Prussian blue. When nitroprusside is exposed to sunlight in a closed vessel, nitric oxide is evolved. It has, however, been observed by the present author that the initial colour change in a dilute aqueous solution of nitroprusside during insolation, from brownish red to a pale yellowish brown, is accompanied by the formation of sodium aquopentacyanoferrate. The latter can be identified by several tests. This substance is formed within 5 to 10 minutes when direct sunlight is used. A longer exposure produces in addition to sodium aquopentacyanoferrate, colloidal Prussian blue.

The catalyst which causes the after-effect has been found to be sodium aquopentacyanoferrate. Several tests are available to detect the formation of sodium aquopentacyanoferrate in a pre-insolated solution of nitroprusside. The latter was mixed with a little dilute aqueous solution of *p*-nitrosodimethylaniline, when a yellow solution was obtained. A little ferrocyanide was added to this mixture in the dark, when an emerald green colouration at once developed. This indicates that ferrocyanide converts aquopentacyanoferrate into aquopentacyanoferrite which is known to react with *p*-nitrosodimethylaniline giving a green colour (Baudisch, 1921). A green colour is also developed in the above mixture when *p*-nitrosodimethylaniline is replaced by dilute sulphuric acid. A direct test for aquopentacyanoferrate is furnished by the starch-iodide reaction. Hofmann (*loc. cit.*) has shown that the former liberates iodine from potassium iodide. A pre-insolated nitroprusside solution was mixed with a little iodide and starch, when a blue iodide of starch was formed. This colour was discharged by thiosulphate. Another reagent which shows that the pre-illuminated pale yellowish brown solution of sodium nitroprusside contains some sodium aquopentacyanoferrate is nitrosobenzene. A little aqueous solution of the sparingly soluble nitrosobenzene was mixed in the dark with pre-insolated

nitroprusside, and then a freshly prepared solution of potassium ferrocyanide was added, when a violet colour was immediately formed. This colour is given by aquopentacyanoferrite, or aquopentacyanoferrate containing some ferrocyanide. This reagent gives a clear indication of the presence of aquopentacyanoferrate in solutions of nitroprusside which have been insolated for 5 to 10 minutes in direct sunlight. It is significant that these tests are not given by mixtures of pre-insolated nitroprusside and ferrocyanide, which have been heated to about 90° C. in the dark for a few minutes before the addition of the enumerated reagents. An alcoholic solution of guaiacum produces a blue colouration with pre-insolated nitroprusside, and the same blue colour is formed with sodium aquopentacyanoferrate. Unilluminated nitroprusside solutions do not give any of these tests, neither does colloidal Prussian blue answer them. It is thus evident that the mechanism of the photochemical after-effect consists in the formation of sodium aquopentacyanoferrate from sodium nitroprusside in light:—

$$Na_2Fe(CN)_5NO + H_2O \xrightarrow{\text{Light}} Na_2Fe(CN)_5H_2O + NO \qquad (I)$$

The aquopentacyanoferrate ions cause catalytic decomposition after darkening as revealed by the after-effect. The autocatalytic nature of the decomposition in the after reaction is reproduced in the dark by aquopentacyanoferrate-uninsolated nitroprusside mixture.

The effect of ferrocyanide in regulating the reaction and producing a high velocity of decomposition follows from the following scheme:—

$$Fe(CN)_5H_2O'' + Fe(CN)_6'''' \rightleftharpoons Fe(CN)_5H_2O''' + Fe(CN)_6''' \qquad (II)$$

Highly reactive aquopentacyanoferrite is produced by interaction of ferrocyanide and aquopentacyanoferrate contained in pre-insolated nitroprusside. In presence of an excess of ferrocyanide, the amount of aquopentacyanoferrite is kept constant and at a high level, to an extent depending upon the concentration of the former. From this it is clear why a uniformly high velocity is obtained in the presence of an excess of ferrocyanide. When smaller amounts of ferrocyanide are used, the velocity constants show a falling off with the progress of the reaction, as the former ions are gradually oxidised, and the equilibrium reaction shifts to the left with a decrease in the concentration of aquopentacyanoferrite ions. It is clear why ferricyanide is not effective in maintaining a rapid rate of decomposition.

Sodium aquopentacyanoferrate is comparatively stable towards heat, whereas sodium aquopentacyanoferrite undergoes a slow spontaneous change in the dark at room temperature. This change is considerably accelerated by heat. This explains why pre-insolated nitroprusside, heated and added

to hydrogen peroxide, does not show lowered reactivity. When a mixture of pre-insolated nitroprusside and ferrocyanide is heated to about 90° C. for a few minutes and then added to hydrogen peroxide, the activity is noticed to diminish considerably, because of the destruction of aquopentacyanoferrite. The same change continues slowly in the dark, and hence a mixture of pre-insolated nitroprusside and ferrocyanide, kept in the dark for some hours before use, shows a lower rate of decomposition than a freshly prepared mixture.

The effect of cyanide ions in suppressing the photochemical after-effect as well as the reaction performed in presence of aquopentacyanoferrate lends support to the mechanism of the photochemical after-effect outlined above. This ' quenching ' effect of cyanide ions is due to the conversion of aquopentacyanoferrate to ferricyanide:—

$$Fe(CN)_5H_2O'' + CN' \rightarrow Fe(CN)_6''' + H_2O \qquad (III)$$

The excess of cyanide ions react with ferricyanide ions to give ferrocyanide ions in the end. The slightly autocatalytic effect noticed in experiments with potassium cyanide is due to the alkali produced by hydrolysis.

When ferrocyanide is first added to pre-insolated nitroprusside, the formation of aquopentacyanoferrite takes place. This is converted by cyanide ions to ferrocyanide ions:—

$$Fe(CN)_5H_2O''' + CN' \rightleftharpoons Fe(CN)_6'''' + H_2O \qquad (IV)$$

The effect of sodium nitrite in suppressing the catalytic activity of the pre-insolated solutions of nitroprusside is to be attributed to the formation of nitroprusside by the interaction of nitrite and aquopentacyanoferrite (Hofmann, *loc. cit.*). The latter is formed when ferrocyanide reacts with aquopentacyanoferrate according to (II). Aquopentacynoferrite reacts with nitrite as follows:—

$$Na_3Fe(CN)_5H_2O + NaNO_2 \rightarrow Na_4Fe(CN)_5NO_2 + H_2O.$$

When nitrite is added to pre-insolated nitroprusside, which has been shown to contain aquopentacyanoferrate, the following reaction takes place.

$$2\ Na_3Fe(CN)_5H_2O + 3\ NaNO_2 + 2\ NaOH = 2\ Na_4Fe(CN)_5NO_2 + NaNO_3 + 3\ H_2O.$$

The quaternary nitroprusside is produced in each case, and as it does not decompose hydrogen peroxide in the dark with a high rate, the photochemical after-effect is ' quenched ' by nitrite. It has been seen that aquopentacyanoferrate or aquopentacyanoferrite reacts with nitrite and the resultant solution gives a purple colour with alkali sulphides showing the conversion of the two substances into nitroprusside. The nitrite-treated pre-insolated nitroprusside, containing ferrocyanide, or aquopentacyanoferrite after

treatment with nitrite does not give the characteristic colour tests mentioned previously, showing the complete conversion of aquopentacyanoferrate and aquopentacyanoferrite into nitroprusside.

Hofmann (*loc. cit.*) has shown that aquopentacyanoferrite is formed when alkaline nitroprusside reacts with hydrogen peroxide. That the addition of alkali to hydrogen peroxide-uninsolated nitroprusside mixture in the presence of ferrocyanide reproduces the photochemical after-effect qualitatively in the dark, and further that the cyanide ions suppress this activity, show that aquopentacyanoferrate causes the after-effect. This furnishes further evidence in support of the mechanism involving the photo-formation of aquopentacyanoferrate from nitroprusside.

The author desires to express his best thanks to Prof. P. S. MacMahon for his kind interest in the work. His thanks are also due to the Lucknow University for the grant of a research fellowship which enabled him to carry out this investigation.

Summary

The photochemical after-effect in the reaction between hydrogen peroxide and sodium nitroprusside is due to the photo-formation of sodium aquopentacyanoferrate. The formation of aquopentacyanoferrate in pre-insolated nitroprusside solution has been proved by qualitative tests. Colloidal Prussian blue does not cause the after-effect.

Pre-insolated nitroprusside continues to react in the dark in the manner indicated by the after-effect. Addition of ferrocyanide causes the reduction of aquopentacyanoferrate to aquopentacyanoferrite, which decomposes hydrogen peroxide with a high velocity. The validity of the suggested mechanism for the after reaction has been tested by the effect of potassium cyanide and sodium nitrite, which have been shown to suppress the after-effect by converting aquopentacyanoferrate to ferrocyanide and nitroprusside respectively. Sodium aquopentacyanoferrate, prepared in the laboratory and added to hydrogen peroxide-uninsolated nitroprusside mixture in the dark in presence and absence of ferrocyanide, has been shown to reproduce the observations obtained by insolation.

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IDEAL THEORY IN BOOLEAN ALGEBRA AND ITS APPLICATION TO DEDUCTIVE SYSTEMS

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The Ideal Theory of the Distributive Lattice and Boolean Rings was initiated by A. Tarski* and developed by M. H. Stone† who in one of his papers points out that Tarski's ' Deductive Systems ' are in fact identical with the additive ideals in the Boolean Algebra of propositions.

In this paper a more detailed study of Ideal Theory of the Boolean Algebra is made with the special object of elucidating the series of concepts and theorems which Tarski advances without proof in his paper.* My treatment of the above involves some new ideas (like Boolean-complements‡ of ideals) and in the proofs I make use of the concepts ' Comprincipal Ideals ' and ' Cut-Complements ' which have been introduced by Dr. Vaidyanathaswamy§ in a recent paper. Thus, the present paper which is devoted to a rapid survey of Ideal Theory in a distributive lattice and in a boolean algebra, it is shown that the notion of the product-complement can be expressed in terms of the Cut-complement and boolean-complement. A continuation of this paper will deal with the application of ideal theory to deductive systems and show incidentally that Tarski's observation that even though the original calculus of propositions may be boolean in nature, yet the structure of deductive systems in that calculus departs from the classical type and conforms to that of Intuitionistic Logic, follows from the fact that the negation¶ of deductive systems corresponds to the product-complement in a distributive lattice whereas the negation of a proposition corresponds to its boolean complement.

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* See A. Tarski, Bibliography.

† M. H. Stone (1). See also M. H. Stone (2). Bibiliography.

‡ We notice that these boolean-complements are different from the Ortho-complements of M. H. Stone (see M. H. Stone 3) which are simply product-complements in a boolean ring.

§ R. Vaidyanathaswamy. Bibliography.

I take this opportunity of expressing my indebtedness to the departmental lectures on "Lattice Theory" recently delivered by Dr. Vaidyanathaswamy (University of Madras).

¶ See A. Tarski. Bibiliography.

1. *Ideals in a Distributive Lattice* L *with* 0 *and* 1

Definition 1. An α-ideal (A_α) is defined as a set of elements of L such that (1) $x \cdot y \epsilon A_\alpha$ whenever $x \epsilon A_\alpha$, $y \epsilon A_\alpha$ (we read $x \cdot y$ *is* in A_α whenever x, y belong to A_α); (2) $x + z \epsilon A_\alpha$ whenever $x \epsilon A_\alpha$, $z \epsilon L$ or alternatively if $x \epsilon A_\alpha$ then all elements $> x$ are in A_α.

Definition 2. A μ-ideal (A_μ) is a set of elements such that (1) $x + y \epsilon A_\mu$ whenever $x \epsilon A_\mu$, $y \epsilon A_\mu$; (2) $x \cdot z \epsilon A_\mu$ whenever $x \epsilon A_\mu$, $z \epsilon L$ or *alternatively* if $x \epsilon A_\mu$, then all elements $< x$ are in A_μ.

Definition 3. If x, y be any two elements of L, then the set of elements $> x$ is easily seen to be an α-ideal which we call the *principal α-ideal defined by* x [denoted by $P_\alpha(x)$], while the set of elements $< y$ is the *principal μ-ideal $P_\mu(y)$ defined by* y.

THEOREM 1. *The α-ideal (μ-ideal*) generated by any sub-set S in L (in other words the smallest α-ideal (μ-ideal) containing S) is the set of elements S_α (S_μ) greater than some finite product, say $S_i \cdot S_j \cdot S_k \cdots S_m$ (less than some finite sum, say $S_i + S_j + S_k + \cdots + S_m$) of the elements of the given set S.*

For, in the first place it is clear that all such elements constitute an α-ideal S_α. Next by def. 1 since any α-ideal A which contains S_α must also contain every finite product $S_i \cdot S_j \cdot S_k \cdots S_m$ of elements of S_α and therefore also any element greater than such a finite product, it follows $A > S_\alpha$ or S_α is the smallest α-ideal which contains S. (Clearly every α-ideal contains 1 and every μ-ideal contains 0.)

Definition 4. The *sum* of a family of α-ideals (μ-ideals) is defined as the α-ideal (μ-ideal) generated by their set-sum.

THEOREM 2. *The sum of a family $\{A, B, C, \cdots\}$ of α-ideals (μ-ideals) is identical with the set of finite products (sums) of elements chosen one from each of the several α-ideals (μ-ideals).*

For, {A, B, C, $\cdots$} being a family of α-ideals, every finite product of elements chosen from A, B, C, $\cdots$ is evidently $>$ than itself and therefore belongs to the ideal generated by S = {A, B, C, $\cdots$}. On the other hand, every element t or of the ideal generated by S = {A, B, C, $\cdots$} can be expressed as such as product; for since by Theorem 1, $t > x_1 \cdot x_2 \cdots x_m$ (where each x belongs to some A) we have $t = t + x_1 \cdot x_2 \cdots x_m = \pi (t + x_i)$ by the distributive law. Hence since $t + x_i$ belongs to the same α-ideal as x_i it

* Substitution of words within brackets give dual theorems for μ-ideals. As the proofs of the latter are exactly similar to the theorems for α-ideals, we prove only the former. In general, we shall denote α-ideals by capital letters, the suffixes being used only when required to distinguish them from μ-ideals. The letter P is used to denote principal ideals.

follows that any element t of S can be expressed as a finite product of elements chosen from the α-ideals A, B, C, $\cdots$. Hence the theorem.

THEOREM 3. *The set K of the common elements of a family* $\{A, B, C, \cdots\}$ *of* α-*ideals* (μ-*ideals*) *is an* α-*ideal* (μ-*ideal*).

(*N.B.*—K_α is not null since it contains 1).

The proof immediately follows from def. 1 and 2. Thus if k_1, k_2 be common elements of A, B, C, $\cdots$ then $k_1 \cdot k_2$ is also a common element and therefore belongs to K_α. Again, any element $> k_1$ is also an element of each of the ideals A, B, C, $\cdots$ and hence of K_α. Hence by def. 1, the set K is an α-ideal. We call K the *product* of the family of α-ideals (μ-ideals).

THEOREM 4. *The product of two* α-*ideals* (μ-*ideals*) *is identical with the set of sums* (*products*) *of pairs of elements chosen from the two* α-*ideals* (μ-*ideals*) *respectively.*

For, if A, B be two α-ideals, then every sum of elements chosen from A, B respectively is a common element of the two ideals; also if t is a common element, then since $t \epsilon A$, $t \epsilon B$, $t = t + t$ and thus every common element of A, B can be expressed as a sum of elements chosen from them. Hence the theorem.

Corollary. The product of any family of α-ideals (μ-ideals) is the set of *existing* sums (products) of the elements chosen one from each of the α-ideals (μ-ideals).

(*N.B.*—The product is non-null since it contains 0).

For, every such existing sum is evidently a common element of the family of α-ideals. *Conversely*, if t be a common element, then it can be expressed as the sum $(t + t + \cdots)$ of elements chosen from them.

It may be noticed that when the ideals are principal the sum and product (which we have defined) of a finite* number of the α- (μ-) ideals conforms to the *lattice-sum* and the *lattice-product* of the elements determining them, thus:—

$$P_\alpha(x) + P_\alpha(y) + P_\alpha(z) + \cdots + P_\alpha(k) = P_\alpha(x \cdot y \cdot z \cdots k)$$
$$P_\mu(x) + P_\mu(y) + P_\mu(z) + \cdots + P_\mu(k) = P_\mu(x + y + z + \cdots + k)$$
$$P_\alpha(x) \cdot P_\alpha(y) \cdot P_\alpha(z) \cdots\cdots\cdots P_\alpha(k) = P_\alpha(x + y + z + \cdots + k)$$
$$P_\mu(x) \cdot P_\mu(y) \cdot P_\mu(z) \cdots\cdots\cdots P_\mu(k) = P_\mu(x \cdot y \cdot z \cdots k).$$

* Even when the infinite product $a, b, c \cdots$ exists and $= k$, it is not necessary that the sum (which always exists by theorem 6) of the principal α-ideals $P_\alpha(a)$, $P_\alpha(b)$, etc., should be $= P_\alpha(k)$; for if such were the case, then any convergent ideal would be principal—which is incorrect (see Theorem 29).

It is easily seen that *an ideal A is the sum of all the principal ideals contained in A.* For, if ϕ be the sum of all the principal ideals contained in A, it is clear that $A > \phi$. But if $x \epsilon A$, then $P(x) < A$ by hypothesis and therefore $P(x) < \phi$. Hence x is contained in ϕ and therefore any element of A is contained in ϕ, *i.e.*, $A < \phi$. Hence $A = \phi$.

2·1. *Structure of the set of α- and μ-ideals in L*

The totality of the α- and μ-ideals form partially ordered systems L_α, L_μ respectively under the ordering relation of 'set-inclusion' ($<$) which is reflexive, transitive and binary. As noticed before for sums and products, this ordering relation conforms to that in L when the ideals are principal. Thus $P_\alpha(x) > P_\alpha(y)$ and $P_\mu(x) < P_\mu(y)$ when and only when $x < y$. The structure of the sets of α- and μ-ideals in L is seen from the following theorems (*viz.*, Theorems 6, 7, 11).

THEOREM 6. *L_α, L_μ are complete lattices,* i.e., *lattices in which unrestricted products and sums exist.*

For, we have shown (Theorems 2, 4) that the sum (product) of a family of ideals is the smallest ideal which contains every ideal of the family (the largest ideal contained in every ideal); therefore the sums and products of any family of ideals which we have defined are lattice-sums and lattice-products respectively. (The 0 of L_α and L_μ is the α-ideal constituted by the element 1 and the μ-ideal constituted by the element 0 respectively; while in both cases, 1 is the whole lattice which is an α- as well as a μ-ideal.)*

THEOREM 7. *L_α, L_μ are complete lattices with completely distributive sums.*

Proof. Let A_i (where i is an ordinal varying over all ordinals $<$ a fixed ordinal γ) be a family of α-ideals in L. Then clearly, $A \cdot \Sigma A_i > \Sigma A \cdot A_i$ so that we have only to show that $A \cdot \Sigma A_i < \Sigma A \cdot A_i$, *i.e.*, to show that any element of $l \cdot s$ is an element of the $r \cdot s$. Now (by Theorem 4) the general element of the $l \cdot s$ is a sum of an element x of A and an element of ΣA_i, *i.e.*, it is of the form $x + y_1 \cdot y_2 \cdots y_m$,—where the y's are elements of the different A's; this by the distributive law $= (x + y_1)(x + y_2) \cdots (x + y_m)$ and since (by Theorem 4) the sums $x + y_i$ belong to the products $A \cdot A_i$, the finite product $\Pi (x + y_i)$ is (by Theorem 4) an element of $\Sigma A \cdot A_i$. Hence the theorem.

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* We notice that when 0 occurs in an equation containing a-ideals it means the a-ideal constituted by the element 1 only, while the O occurring in an expression consisting of μ-ideals is the ideal constituted by 0 only.

Corollary. All finite sums are distributive and hence* all finite products are distributive so that L_α, L_μ are distributive lattices which are complete and possess completely distributive sums.

2·2. *Product-Complements*† *in a Distributive Lattice* L *with* 0 *and* 1

Definition 5. The *product-complement* (*sum-complement*) of an element a is defined as an element a' such that $a\cdot a'=0$ $(a+a'=1)$ *and* for *all* x, $a\cdot x=0: \supset : x<a'$ $(a+x=1: \supset : x>a')$.

[If the product-complement (sum-complement) exists, it is necessarily unique.]

Follow some important properties of product-complements:

THEOREM 8. $a<b$ *implies* $A'>B'$.

For, since $b\cdot b'=0$ and $a<b$, $a\cdot b'<b\cdot b'=0$ or $a\cdot b'=0$ whence (by def. 5) $b'<a'$ or $a'>b'$.

THEOREM 9. (*i*) $A<A''$; (*ii*) $a'''=a'$.

(i) Since $a\cdot a'=0$, $a<a''$.

(ii) Substituting a' for a in (i) we have $a'<a'''$; again, putting $b=a''$ in Theorem 8, we obtain $a'''>a'$ so that $a'''=a'$.

THEOREM 10. *If* Σa *exists, then* $\pi a'$ *exists and* $=(\Sigma a)'$.

For, since $\Sigma a>a$, $(\Sigma a)'<a'$ (from Theorem 8) for every a in the sum; but if an element is $<$ any a', it must be $<$ the product-complement of the totality of the a's, *i.e.*, $<(\Sigma a)'$. For, let $x<a'$; then (from Theorem 8, 9 (i) respectively) $x'>a''>a$ so that $x'>a$. Hence, $x'>\Sigma a$ implies $x''<(\Sigma a)'$ which together with $x<x''$ implies $x<(\Sigma a)'$. Therefore $(\Sigma a)'$ is by def. 5 the product $\Pi a'$.

(When there are only two elements, $(a+b)'=a'\cdot b'$).

We remark the dual of the above property, *viz.*, if Πa exists, then $\Sigma a'$ exists and $=(\Pi a)'$ is not true for the general lattice but can be shown to be valid when L becomes a boolean algebra **B**.

THEOREM 11. *Each element of a complete lattice* (*in particular* L_α *or* L_μ) *with completely distributive sums possesses a product-complement.*

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* However in a complete lattice the distributivity of infinite products do not follow from the distributivity of all sums. See H. M. MacNeille. Bibliography.

† For a more detailed treatment of product-complement, Simple and Normal elements in a distributive lattice, see MacNeille (Bibliography or my paper entitled "On the Formal Structure of the Propositional Calculus—1," to appear shortly in the *Journal of the Indian Mathematical Society*.

Proof. For, since the product and sum of all elements (which exists by the hypothesis that the lattice is complete) are 0 and 1 of the lattice, it is clear that a complete lattice contains both 0 and 1. Now, the set S_x of all elements x such that $a \cdot x = 0$ is not null (since $x = 0$ is such an element) and the sum $a' = \Sigma x$ of all such elements exists since the lattice is complete; this sum being distributive by hypothesis, $a \cdot a' = a \cdot \Sigma x = \Sigma a \cdot x = 0$. Further (by def. 5), since a' is the sum of all the x's in question, $a \cdot x = 0$ implies $x < a'$. Thus a' is the product-complement of a.

It follows that in particular (by Theorems 6, 7) every α- or μ-ideal in a distributive lattice L has a product-complement which is an α- or μ-ideal respectively.

When the ideals are principal, we have:

THEOREM 12. *If* a, a′ *are sum-complements* (*product-complements*) *in L, then the principal* α*-ideals* (μ*-ideals*) *defined by* a, a′ *are product-complements in* L_α (L_μ) *and the converse.*

For, let a, a' be sum-complements in L so that $P_\alpha(a) \times P_\alpha(a') = P_\alpha(a + a') = P_\alpha(1) = 0$. Again if X is an arbitrary α-ideal, such that $X \cdot P_\alpha(a) = 0$, then for every element $x \epsilon X$, $a + x = 1$. Thus (by definition of sum-complements) $x > a'$. Therefore $x \epsilon P_\alpha(a')$. Since this is true for every element x, $X < P_\alpha(a')$ so that $P_\alpha(a')$ is the product-complement of $P_\alpha(a)$.

2·3. *Simple and Normal Elements in L*

In a lattice in which every element a has a product-complement a', we have the following:

Definition 6. The element a is said to be *normal* if $a'' = a$ and it is said to be *simple* if $a + a' = 1$.

THEOREM 13. *Every simple element in L is a normal element.*

For, if a is simple, then $a + a' = 1$ so that $a'' = a'' \cdot (a + a) = a \cdot a''$ or $a'' < a$; but since $a'' > a$, we have $a'' = a$.

THEOREM 14. *Sums, products and product-complements of simple elements are simple*; *if* a, b *are simple, then* $(a \cdot b)' = a' + b'$.

(The proofs are immediate by simple algebraic manipulations.)

THEOREM 15. *The set of normal elements is identical with the set of product-complements.*

For, if $a = a''$ then a is the product-complement of a'; and if b' is the product-complement of b, then $b' = b''' = (b')''$ so that any product-complement is normal.

THEOREM 16. a *is normal if and only if* a′<b *implies* a> b′ *for all* b *or* a′<b′ *implies* a> b *for all* b.

For, if $a = a''$, then $a' < b$ implies $a'' > b'$ which implies $a > b'$; again $a' < b'$ implies $a'' > b''$ which implies $a > b$.

If $a \neq a''$, on putting $b = a'$, $b = a''$ respectively, the implications are seen to be false.

THEOREM 17. $(a \cdot b)'$ *is the smallest normal ideal containing* a′ *and* b′.

For, if $a' = b'$ then $a \cdot x = 0$ implies and is implied by $b \cdot x = 0$ and *vice versa*. Hence since x is arbitrary, $ac \cdot x = 0$ implies and is implied by $bc \cdot x = 0$ whence we have $(ac)' = (bc)'$. So that $a' = b'$ implies $(ac)' = (bc)'$. Next if $a' = b'$, $c' = d'$, then clearly $(ac)' = (bc)' = (bd)'$. Therefore since $a' = a'''$, $b' = b'''$, we have $(ab)' = (a'' \cdot b'')' = (a' + b')''$. But $(a' + b')''$ is a normal element $> a'$ and $> b'$; and if n is a normal element $> a'$ and $> b'$ then n must be $>$ than $a' + b'$ so that $n = n'' > (a' + b')''$. Hence, $(a \cdot b)'$ is the smallest normal element containing a' and b'.

3·0. *The Theory of α- and μ-ideals in a Boolean Algebra*

We next proceed to study the nature of the lattices $\mathbf{B}_\alpha$, $\mathbf{B}_\mu$ when the distributive lattice L becomes a boolean algebra **B**. The conditions for a distributive lattice L to be a boolean algebra **B** are: (1) every element a possesses a product-complement* a', (2) every element is simple and therefore normal (consequently both the equations $(a + b)' = a' \cdot b'$ *and* $(a \cdot b)' = a' + b'$ are valid in **B**). Therefore, the boolean complement a' of a is both the sum and product-complement of a so that the principal ideals $\mathbf{P}_\alpha(a)$, $\mathbf{P}_\alpha(a')$, $[(\mathbf{P}_\mu(a), \mathbf{P}_\mu(a')]$ are product-complements in $\mathbf{B}_\alpha$ $(\mathbf{B}_\mu)$. (See Theorem 12.)

Definition 7. An ideal A in the lattice of ideals is said to be *neutral* if (A) is distributed by every product.

Definition 8. The intersection of any family of principal ideals is called a *comprincipal ideal*.†

The characteristic features of the ideal theory of **B** as contrasted with that of the general distributive lattice L are three, namely:

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* From Theorem 11, evidently B_α, B_μ necessarily possess product-complements.

† This concept and that of the cut-complement (see Theorem 22) defined for partially ordered sets by Dr. Vaidyanathaswamy, are equally valid for distributive lattices and hence also for boolean algebras.

(1) *The set of *simple* ideals is identical with the set of *principal* ideals (Theorem 19).

(2) *The set of *normal* ideals is identical with the set of *comprincipal* ideals (Theorem 25).

(3) The set of *principal* ideals is identical with the set of *neutral* ideals (Theorems 26, 27).

3·1. *Boolean Complements, Simple and Principal Ideals*

THEOREM 18. *The set $\bar{A}$ of (boolean) complements of elements of an α-ideal A (μ-ideal A) constitutes a μ-ideal (α-ideal) which we call the boolean-complement of the ideal A.*

For, if x, y be two elements of an α-ideal ($\mathbf{A}_\alpha$) and x', y' their boolean complements, then since **B** is a boolean algebra, $x' + y' = (x \cdot y)'$. But since $x \cdot y \epsilon \mathbf{A}_\alpha$, $x' + y' = (x \cdot y)' \epsilon \bar{\mathbf{A}}$. Further if $k < x'$ then $k' > x'' > x$ and therefore $k' \epsilon \mathbf{A}$. Hence, $k = k'' (< x') \epsilon \bar{\mathbf{A}}$, so that $\bar{\mathbf{A}}$ is a μ-ideal.

Corollary (i). $\bar{\bar{\mathbf{A}}} = \mathbf{A}$; $\bar{\bar{\bar{\mathbf{A}}}} = \bar{\mathbf{A}}$.

The relation between an ideal A and its boolean-complement $\bar{\mathbf{A}}$ is obviously a symmetrical one since each consists of the boolean-complements of all the elements of the other. Therefore, $\mathbf{A} = \bar{\bar{\mathbf{A}}}$. And since $\mathbf{A} = \bar{\bar{\mathbf{A}}}$, $\bar{\mathbf{A}} = \bar{\bar{\bar{\mathbf{A}}}}$.

Corollary (*ii*). $\overline{\mathbf{P}_\alpha(a)} = \mathbf{P}_\mu(a')$; $\overline{\mathbf{P}_\mu(a)} = \mathbf{P}_\alpha(a')$.

Corollary (*iii*). $\overline{\Sigma \mathbf{A}} = \Sigma \bar{\mathbf{A}}$; $\overline{\Pi \mathbf{A}} = \Pi \bar{\mathbf{A}}$.

Proof. We assume the A's to be α-ideals so that their boolean-complements $\bar{\mathbf{A}}$'s are μ-ideals. Now, the general element of $\overline{\Sigma \mathbf{A}}$ ($\overline{\Pi \mathbf{A}}$) is the boolean complement of an element of $\Sigma \mathbf{A}$ ($\Pi \mathbf{A}$) which element (by Theorems 2, 4) is a finite product (sum) of elements chosen from the A's. Therefore, the general element of $\overline{\Sigma \mathbf{A}}$ ($\overline{\Pi \mathbf{A}}$) is the boolean-complement of a finite product (sum) of elements chosen from the A's, *i.e.*, it is a finite sum (product) of the boolean-complements of elements belonging to the A's so that the general element of $\overline{\Sigma \mathbf{A}}$ ($\overline{\Pi \mathbf{A}}$) belongs to $\Sigma \bar{\mathbf{A}}$ ($\Pi \bar{\mathbf{A}}$). *Conversely*, it can be

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* M. H. Stone's characterisations of totally additive and totally multiplicative boolean rings [see M. H. Stone (3)] may be easily derived from these theorems. Thus a totally additive boolean ring must have a unit and is therefore a boolean algebra, and (by Theorem 7) must also be totally multiplicative. Hence, the comprincipal ideals reduce to principal ideals and therefore the normal ideals are identical with principal ideals — which is Stone's characterisation.

Again, a totally multiplicative boolean ring can by adjoining a unit [see M. H. Stone (2)] be made into a complete boolean algebra and therefore it is easy to deduce Stone's theorem, *viz.*, " principal ideals coincide with normal ideals ".

proved in the same way that any element of $\Sigma\overline{A}$ ($\Pi\overline{A}$) is an element of $\Sigma\overline{A}$ ($\Pi\overline{A}$) and hence the corollary.

THEOREM 19. *The set of simple ideals in* **B** *is identical with the set of principal ideals.*

Proof. Considering α-ideals, we prove first that every principal ideal is simple. If a, a' are boolean-complements (by Theorem 12), $P_\alpha(a)$, $P_\alpha(a')$ are product-complements and $P(a)+P(a')=P(a\times a')=P(0)=1$. Hence any principal ideal $P_\alpha(a)$ is simple. *Conversely*, to prove that any simple ideal of **B** is principal, let A be a simple α-ideal and A′ its product-complement so that $A+A'=1$. This implies that any element of the lattice can be expressed as a product of elements chosen from A, A′; therefore there exist $x\epsilon A$, $y\epsilon A'$ such that $x\cdot y=0$. If z be an arbitrary element of A, then (by def. 5), $z+y=1$ for all $y\epsilon A'$. Hence $z=z+0=z+x\cdot y=(z+x)(z+y)=z+x$ (since $z+y=1$), *i.e.*, $z>x$. Since this is true for any element z of A, A is the principal α-ideal definied by x.

This theorem can be generalised as follows:

THEOREM 20. *If M, N are two ideals such that $M+N$, $M\cdot N$ are principal, then M, N are principal.*

Proof. Suppose M, N are α-ideals and let $M+N=P(a)$, $M\cdot N=P(b)$. It is shown first that there exist elements x, y; $x\epsilon M$, $y\epsilon N$ such that $x\cdot y=a$, $x+y=b$. Now, (by theorems 2, 4) there exist ξ_1, ξ_2 in M, η_1, η_2 in N such that $\xi_1\cdot\eta_1=a$; $\xi_2+\eta_2=b$. Then, $\xi_1\xi_2\cdot\eta_1\eta_2<\xi_1\eta_1=a$ *and* $\xi_1\xi_2+\eta_1\eta_2<(\xi_2+\eta_2)=b$. But since $\xi_1\xi_2\epsilon M$, $\eta_1\eta_2\epsilon N$ (by Theorems 2, 4), $\xi_1\xi_2\cdot\eta_1\eta_2\epsilon P(a)$; $\xi_1\xi_2+\eta_1\eta_2\epsilon P(b)$ so that $\xi_1\cdot\xi_2\cdot\eta_1\eta_2=a$; $\xi_1\xi_2+\eta_1\eta_2=b$. Thus there exist $x=\xi_1\xi_2$ in M, $y=\eta_1\eta_2$ in N such that $x\cdot y=a$, $x+y=b$. Now, if t be an arbitrary element of M, then since $t>a$, $t=t+a=t+x\cdot y=(t+x)(t+y)$. But since $y<(x+y)=b$, $(t+y)<(t+b)$; also since $t+y$ is an element of $M\cdot N=P(b)$, $t+y>b$ and again, $t+y>t$. Therefore, $t+y=t+b$. Hence, $t+y=t+b=t+(x+y)>t+x$, whence $t=(t+x)(t+y)=t+x$ or $t>x$. Since this is true for any element t of M it follows that M is the principal α-ideal defined by x. In the same way, we can show that N is the principal α-ideal defined by y.

3·2. *Comprincipal Ideals and Cut-Complements*

THEOREM 21. *A comprincipal ideal A is the intersection of all the principal ideals containing it.*

For, let the comprincipal ideal A be the intersection of a family (P_i) of principal ideals. Also, let the intersection of all the principal ideals containing A be A′. We have to show that $A=A'$. Clearly, $A'>A$ and

since $A' = \Pi (P_i)$ X the product of other principal ideals containing A, we have $A' < \Pi (P_i) = A$. Thus the theorem is proved.

Definition 9. Given an ideal A, the *comprincipal envelope* of A is defined as the intersection of all principal ideals containing A.

Corollary (i). The comprincipal envelope of A is the smallest comprincipal ideal containing A.

For, a comprincipal ideal K containing A must be the intersection of a family of principal ideals containing A and hence must contain the comprincipal envelope of A which is the intersection of *all* principal ideals containing A.

As a consequence of definition (9) and corollary (i), Theorem 21 can be re-stated as follows:

Corollary (ii). *A comprincipal ideal is its own comprincipal envelope.*

THEOREM 22. *The set A_c of all elements $<$ ($>$) than every element of an α-ideal A (μ-ideal A) is a comprincipal μ-ideal (α-ideal) which we call the cut-complement of A.*

For, if $x \epsilon A_c$, $y \epsilon A_c$ then obviously $x + y \epsilon A_c$ and $x \cdot k < x$ is also in A_c. Thus A_c is a μ-ideal. Further, A_c is comprincipal because it is clearly the intersection of the principal μ-ideals defined by the elements of A.

Corollary (i). $(A_c)_c = A_{cc}$ is the comprincipal envelope of A.

Since A_{cc} is the cut-complement of A_c it is comprincipal, further (A being an α-ideal) A_{cc} being the cut-complement of A_c, it is the intersection of all the principal α-ideals defined by elements of A_c. But these are precisely the principal α-ideals which contain A. Hence A_{cc} is the intersection of all the principal α-ideals containing A, *i.e.*, it is the comprincipal envelope of A.

Corollary (ii). $A_{cc} = A$ if and only if A is comprincipal.

The first part is cor. (ii) of Theorem 21. As for the converse, we have only to observe that if A is not comprincipal, then it cannot be equal to the comprincipal ideal A_{cc}.

Corollary (iii). $A_{ccc} = A_c$ *or* the cut-complement of the comprincipal envelope of A is identical w th the cut-complement of A.

Putting $A = A_c$ in (ii), we get A_{ccc} as the comprincipal envelope of A_c. But A_c, as the cut-complement of A is comprincipal. Therefore (by ii), $A_{ccc} = A_c$.

THEOREM 23.* $(\Sigma A)_c = \Pi A_c$.

---

* The dual of this theorem, namely, $-(\Pi A)_c = \Sigma A_c$ cannot be proved by this method and is not true; we can only show that $(\Pi A)_c > \Sigma A_c$.

If the A's are α-ideals so that A_c's are μ-ideals, any element of the product $\Pi A_c <$ every element of A, every element of B, $\cdots$ and hence $<$ every element of ΣA, so that we have $\Pi A_c < (\Sigma A)_c$. Similarly, any element of $(\Sigma A)_c <$ all elements of (ΣA) and therefore $<$ every element of A, every element of B, etc. Hence, $(\Sigma A)_c < \Pi A_c$ so that $(\Sigma A)_c = \Pi A_c$.

3·3. *Relation between the Cut-complement, Boolean-complement and Product-complement*

We have defined so far, three operations on ideals in **B**, *viz.*, boolean-complement, cut-complement and product-complement; the first two change the species of ideals (*i.e.*, α-ideals to μ-ideals and *vice versa*) while the last preserves the species.

The connection between these three operations can be stated thus:

THEOREM 24. *The product-complement of an ideal is the cut-complement of its boolean-complement as well as the boolean-complement of its cut-complement* [*in Symbols*, $A' = (\bar{A})_c = \overline{(A_c)}$.]

Proof. Let A be an α-ideal, $\bar{A}$ its boolean-complement and $(\bar{A})_c$ the cut-complement of $\bar{A}$. We have to show that (1) if $x \epsilon A$, $y \epsilon (\bar{A})_c$, $x + y = 1$ and (2) if $A \cdot X = 0$ then $X < (\bar{A})_c$. To prove (1), if x' be the boolean-complement of x (ϵA) then $x' \epsilon \bar{A}$ and if $y \epsilon (\bar{A})_c$, then $y >$ every element of $\bar{A}$ so that in particular $y > x'$. Therefore, $y + x > x + x' = 1$; hence $x + y = 1$ for all x in A and all y in $(A)_c$ and therefore $A \cdot (\bar{A})_c = 0$. Next to prove (2), if $A \cdot X = 0$ and $x \epsilon X$, then for all $y \epsilon A$, $x + y = 1$ or $x > y'$ for all $y \epsilon A$. But as y varies in A, y' ranges over all elements of $\bar{A}$. Therefore $x \epsilon (\bar{A})_c$. Since $x \epsilon X$ is arbitrary, this shows $X < (\bar{A})_c$. Thus $(\bar{A})_c$ is the product-complement of A.

We complete the proof of the theorem by showing that the boolean-complement of the cut-complement of A is identical with the cut-complement of the boolean-complement of A [*i.e.*, $\overline{(A_c)} = (\bar{A})_c$]. For, the proposition $y \epsilon (\bar{A})_c \equiv$ the proposition $(x)\{x \epsilon A ; \supset : y > x'\}$. And the proposition $y \epsilon \overline{(A_c)} \equiv$ the proposition $y' \epsilon A_c \equiv (x)\{x \epsilon A : \supset : y' < x\}$. But since the proposition $y > x' \equiv$ the proposition $y' < x$, the above two statements are logically equivalent and therefore we have $\overline{(A_c)} = (\bar{A})_c$.

Corollary (i). Every product-complement is comprincipal and *conversely* every comprincipal ideal is the product-complement of some ideal.

For, since Theorem 24 exhibits the product-complement of an ideal as the cut-complement of its boolean-complement, it follows (by Theorem 22) that all product-complements are comprincipal. *Conversely*, if an ideal M is comprincipal, it is the cut-complement of some ideal A (in particular,

by Theorem 22 we can take $A = M_c$) so that (by Theorem 18, cor. 1), $A_c = (\overline{\overline{A}})_c =$ the product-complement of the ideal $\overline{A}$ by Theorem 24.

Corollary (ii).* $(\Sigma A)' = \Pi A'$.

For, $(\Sigma A)' = (\overline{\Sigma \overline{A}})_c = (\Sigma \overline{A})_c = \Pi (\overline{A})_c = \Pi A'$ (by Theorem 24, cor. (iii) of Theorem 18, Theorem 23 and Theorem 24 respectively).

Corollary (*iii*). The product of any number of normal elements is normal.

THEOREM 25. *The set of normal ideals is identical with the set of comprincipal ideals.*

Proof. We have already seen (Theorem 15) that in $\mathbf{B}_a$ or $\mathbf{B}_\mu$ the set of normal elements is identical with the set of product-complements; these product-complements (by cor. (i), Theorem 24) are identical with the set of comprincipal ideals. Hence the set of normal ideals is identical with the set of comprincipal ideal.

Corollary. A'' is the comprincipal envelope of A.

Now, A'' is known to be the smallest normal ideal containing A (or the normal envelope of A); for, in the first place, A'' is a product-complement and therefore normal. And if X be a normal ideal containing A, then $X' < A'$ so that $X = X'' > A''$; therefore, A'' is the smallest comprincipal ideal containing A, *i.e.*, (by cor. (i) of Theorem 21) it is the comprincipal envelope of A.

3·4. *Neutral Ideals*

THEOREM 26. *Principal Ideals are neutral.*

Proof. We have to show that if $P(x)$ is a principal α-ideal and $\{A\}$ any family of α-ideals of which A is a typical member, then

$$P(x) + \Pi(A) = \Pi(P(x) + A).$$

Lemma. We first prove that $P(x) + Y$ is identical with the set of elements t such that $(t + x') \in Y$. For, let $x' + t \in Y$. Then since $t + x \in P(x)$ and $(t + x') \in Y$ by hypothesis, it follows that $t = (t + x)(t + x') \in (P(x) + Y)$. *Conversely*, if $t \in P(x) + Y$ then (by Theorem 2), $t = x_1 a_1$ where $x_1 (> x) \in P(x)$ and $a_1 \in Y$; therefore, $t + x' = x_1 a_1 + x' = (x' + a_1)\cdot(x' + x_1) = x' + a_1$ (since $x' + x_1 > x + x' = 1$) $\in Y$. Thus $P(x) + Y$ is the set of all elements t such that $(t + x') \in Y$.

Hence it follows by putting $Y = \Pi(A)$ in the lemma, that $P(x) + \Pi(A)$ is the set $S(t)$ of all elements t such that $(t + x') \in \Pi A$. Therefore this set $S(t)$ is the set-product (and therefore the ideal-product) of the sets $S_A(t)$,

* The dual result, *viz.*, $(\Pi A)' = \Sigma A'$ cannot be obtained for the reason expressed in the f.n. under Theorem 23.

$S_B(t), \cdots$ where $S_A(t)$ is the set of elements t such that $(t + x') \epsilon A$, so that by the lemma $S_A(t)$ is identical with the ideal $P(x) + A$. Similarly $S_B(t)$ is identical with $P(x) + B$; etc. Hence, $P(x) + \Pi(A) = \Pi(P(x) + A)$.

THEOREM 27. *Neutral Ideals are principal.*

Proof. To prove this, it is sufficient to show that if A is not principal, then there exists one product which does not distribute it.

Now, any ideal A is the sum of all the principal ideals $(P(x), x \epsilon A)$ contained in it so that (by cor. (ii) Theorem 24) $A' = \Pi P(x')$. Hence, $A + \Pi P(x') = A + A' \neq 1$ (by Theorem 19). But since $A > P(x)$, $[A + P(x')] > [P(x) + P(x')]$ which $= 1$. Hence, $\Pi [A + P(x')] = 1 \neq A + \Pi P(x')$. Thus the product $\Pi P(x')$ does not distribute A, hence the theorem.

The following theorem is a consequence of the above two results.

THEOREM 28. *$A + D$ is normal for all normal ideals D if and only if A is principal.*

Proof. First let A be principl. Then since (by Theorems 25, 26, 27 respectively) every normal ideal D is comprincipal (and therefore = a product ΠP of principal ideals) and every principal ideal is neutral, we have $A + D = A + \Pi P = \Pi(A + P)$ which being the product of principal ideals $A + P$, is comprincipal, and therefore (by Theorem 25) normal; so that $A + D$ is normal for all normal ideals D. *Conversely*, if A is not principal, we can find normal ideals D such that $A + D$ is not normal; *e.g.*, since A is not principal (by Theorem 19) it cannot be simple so that $A + A' \neq 1$. But $(A + A')'' = 1$. Hence $A + A'$ is not normal even though A' is normal.

3·5. *Convergent Ideals.*

Definition 10. An α-ideal (μ-ideal) is said to be convergent if the product (sum) of all its elements exists.

THEOREM 29.* *An ideal A is convergent if and only if any one of the following conditions is satisfied*:

(i) *A_c is principal.*

(ii) *$\bar{A}$ is convergent.*

(iii) *A' is principal.*

(iv) *A'' is principal.*

(v) *The comprincipal envelope of A is principal.*

(vi) *$A' + D' = (A \cdot D)'$ for every ideal D.*

(vii) *$A'' + D'' = (A + D)''$ for every ideal D.*

---

* This theorem *ad verbatim* corresponds to Satz 26 of Tarski's (see A. Tarski).

Proof. As usual, we prove the theorem for α-ideals.

(i) If A be a convergent α-ideal, A_c its cut-complement and if the product of all its elements (which exists by hypothesis) $= K$, then (by Theorem 22) every element of $A_c < K$ and also since $K <$ every element of A, $K \epsilon A_c$; hence A_c is the principal μ-ideal defined by K. *Conversely*, if A_c is principal {say $P_\alpha(k)$} then since $K <$ every element of A and since every element of A_c (in other words every element $<$ every element of A) $< K$, K satisfies def. 10 of 'product of all elements of A'. Hence A is convergent.

(ii) Since A is a convergent α-ideal, by def. 10 the product (ΠA) of all elements of A exist; and because **B** is a boolean algebra (according to the remark made at the end of Theorem 10), $\Sigma a'$ exists and $= (\Pi a)'$; hence $\bar{A}$ is convergent. *Conversely*, if $\bar{A}$ be assumed to be convergent so that Σa exists, then (by the above-mentioned theorem), $\Pi a'$ exists and $= (\Sigma a)'$; therefore A is convergent.

(iii) If A is convergent, then [by (ii)] $\bar{A}$ is convergent and hence $A' = (\bar{A})_c$ is principal [by (i)]; *conversely*, if A' is principal, *i.e.*, (by Theorem 24) $\overline{(A_c)}$ is principal, then A_c is principal [by cor. (ii), Theorem 18] and hence A is convergent.

(iv) and (v) Since (by corollary of theorem 25) A'' is the comprincipal envelope of A, we have only to show that if A is convergent, A'' is principal and *vice versa*. This is immediately seen; for if A is convergent, then [from (iii)] A' is principal and therefore A'' is principal. *Conversely*, if A'' is principal, then $A' (= A''')$ is principal and hence [from (iii)], A is convergent.

(vi) Let $A' + D' = (A \cdot D)'$ for all D; to show A is convergent. Now (by Theorem 17) $A' + D' = (AD)' = (A' + D')''$ so that $A' + D'$ is normal for all normal ideals D'. Hence (by Theorem 28) A' is principal so that [by (iii)] A is convergent. *Conversely*, if A is convergent, then since A' is principal and D' normal, (by Theorem 28) $A' + D'$ is normal for all D' whence $A' + D' = (A' + D')'' = (AD)'$.

(vii) Given A to be convergent, we have to show $A'' + D'' = (A + D)''$ for all D.

Now, since A is convergent, A', A'' are [by (iii) and (iv)] principal. Hence since D'' is normal (by Theorem 28), $A'' + D''$ is normal for all D, *i.e.*, $A'' + D'' = (A'' + D'')'' = (A'''D''')' = (A'D')' = (A + D)''$ [by def. 6, by Theorem 24, cor. (ii), by Theorem 24, cor. (ii) respectively].

Conversely, if $A'' + D'' = (A + D)''$ for all D, to prove A is convergent.

Now, as before $(A+D)''=(A'\cdot D')'=(A'''\cdot D''')'=(A''+D'')''$ so that we have $(A''+D'')=(A''+D'')''$ whence $A''+D''$ is normal for all D, and since D'' is normal (by Theorem 28), A'' is principal, *i.e.*, A is convergent.

THEOREM 30. *If A, D are convergent, then $A+D$, $A\cdot D$ are convergent.*

For, since A, D are convergent [by Theorem 29 (iii)], A', D' are principal. Now in order to prove $A+D$, $A\cdot D$ are convergent, we have to show $(A+D)'$, $(A\cdot D)'$ are principal, which is immediately seen; for by (vi), $(A\cdot D)'=(A'+D')$ which is principal (since A', D' are principal); and again [by Theorem 24, cor. (ii)], $(A+D)'=A'\cdot D'$ which is also principal. Hence the theorem.

THEOREM 31. *If $A+D$ is principal, $A\cdot D$ is convergent, then A, D are convergent.*

Proof. For, a principal ideal contains the comprincipal envelope of any ideal which it contains; hence since $A+D$ is principal it follows (by corollary of Theorem 25) that $A+D>A''$, $A+D>D''$ so that $A+D>A''+D''$. But since $A''>A$, $D''>D$ we have $A''+D''>A+D$. Hence,

$$A''+D''=A+D=\text{a principal ideal} \qquad (1)$$

But since (by hypothesis) $A\cdot D$ is convergent, $(A\cdot D)'$ is [by Theorem 29 (iii)] principal; and $(A\cdot D)'=(A''\cdot D'')'=\overline{(A''\cdot D'')}_c$ (by theorems 17, 24 respectively) so that $\overline{(A''\cdot D'')}_c$ is principal. Therefore, since if the boolean-complement of an ideal is principal the ideal itself is principal, it follows that $(A''\cdot D'')_c$ is principal. But since $A''\cdot D''$ is normal, it is comprincipal (by Theorem 25) and also, if the cut-complement of a comprincipal ideal X is principal then [from Theorem 22, cor. (ii)] X itself is principal, *i.e.*, $A''\cdot D''$ is principal. (2)

Therefore from (1) and (2) by Theorem 21, we obtain A'', D'' to be principal and hence [by Theorem 29 (ii)] A, D are convergent.

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